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TEMPERATURE AND THE COMPTON EFFECT

By G. E. M. Jauncey and H. Bauer
Washington University, St. Louis

(Received May 25, 1929)

Abstract

The intensity of x-rays diffusely scattered by crystals should increase with the temperature according to Debye. It is to be expected that these scattered rays of Debye would be unmodified. Hence the ratio of modified to unmodified rays may decrease with the temperature. Debye's argument applies to powdered crystals and therefore to so-called amorphous substances. The effect of temperature on this ratio has therefore been examined. Using DeFoe's method an aluminum absorbing sheet was transferred from the primary to the scattered beam and the ratio of the two ionization currents found at temperatures of −140°C, 25°C and 565°C. Wave-lengths ranging from 0.32A to 0.62A were scattered by carbon at angles of 60°, 75° and 90°. Also x-rays were scattered from aluminum and copper at angles of 90° and 130°. In each case the difference between the ratios at the different temperatures was not greater than the probable error, implying that there is no effect of temperature on the ratio of modified to unmodified rays in the Compton effect.

1. Introduction

Debye[1], Waller,[2] and Waller and James[3] have shown that a decrease of the intensity of x-rays regularly reflected from crystals with increase of temperature is to be expected. This expectation has been realized in the experiments of Bragg,[4] Backhurst,[5] James and Firth[6] and others. Debye's theory further requires that the regular reflection from crystals should be accompanied by diffuse scattering at all angles and that the intensity of the diffusely scattered rays should increase with increase of temperature. This question of the increase of the intensity of the diffusely scattered x-rays was examined experimentally by Jauncey,[7] who found that the intensity varied much more slowly with the temperature than predicted by Debye's formula. Jauncey[8] also found that the diffusely scattered rays were softer than the

[1] P. Debye, Ann. d. Physik **43**, 49 (1914).
[2] I. Waller, Zeits. f. Physik **17**, 398 (1923).
[3] Waller and James, Proc. Roy. Soc. **A117**, 214 (1927).
[4] W. H. Bragg, Phil. Mag. **27**, 881 (1914).
[5] I. Backhurst, Proc. Roy. Soc. **A102**, 340 (1922).
[6] James and Firth, Proc. Roy. Soc. **A117**, 62 (1927).
[7] G. E. M. Jauncey, Phys. Rev. **20**, 421 (1922).
[8] G. E. M. Jauncey, Phys. Rev. **20**, 405 (1922).

primary rays and therefore probably consisted of both unmodified and modified rays. Since the intensity of the diffusely scattered rays varies more slowly with the temperature than predicted by Debye's theory, it might be supposed that these rays consist of two parts: one part whose intensity depends on the temperature according to Debye's formula and a second part whose intensity is either independent of the temperature or varies with the temperature in a different way from that required by Debye's formula. It is not unreasonable to suppose that the first part consists of unmodified rays, because this part is explained on the principles of the classical theory; and that the second part consists of modified rays. If this is so, the intensity of the unmodified rays should increase with temperature. Just how the intensity of the modified rays should vary with the temperature is uncertain. Since the modified rays are scattered mainly from the loosely bound electrons, and since it is possible that the number of these electrons is constant with the temperature or, at any rate, varies in a different way with the temperature from Debye's formula, the intensity of the modified rays should vary differently with the temperature than should the intensity of the unmodified rays. It is to be expected, therefore, that the ratio of the intensities of the modified and unmodified rays scattered at a given angle by a crystal will depend on the temperature of the crystal.

It is known that many solid substances such as aluminum consist of minute crystals and therefore act towards x-rays as powdered crystals. Collins[9] has shown that the intensities of the powdered crystal spectrum lines produced by a sheet of aluminum vary qualitatively with the temperature according to Debye's formula. Hence it would seem that the ratio of the intensities of the modified and unmodified scattered x-rays in the Compton effect should vary with the temperature. The present research was therefore undertaken, and we have examined the effect of varying the temperature from $-140°C$ to $565°C$ on this ratio for carbon, aluminum and copper as the scatterer.

2. Apparatus and Experimental Method

The source of voltage consisted of two motor-generator sets. The first set comprised a 3 phase, 60 cycle, 220 volt induction motor, which was driven by the local power supply, and a 110 volt d.c. generator with a voltage regulator connected to the field coils. This steady d.c. voltage was then applied to the d.c. motor of the second motor-generator set, the a.c. generator of which supplied very constant 110 volt, single phase current to the primary coil of the x-ray transformer. The high voltage applied to the x-ray tube was rectified by means of a kenotron. With this arrangement it was found that the rate of radiation from the x-ray tube remained remarkably constant.

The method of obtaining the ratio of the modified to the unmodified intensities was similar to that used by De Foe[10] with the exception that a direct deflection instead of a balance method was used. Referring to Fig. 1, the x-rays entered the heating, or cooling, chamber C through a thin mica window. The x-rays were then scattered by a block of the scattering sub-

[9] E. H. Collins, Phys. Rev. **24**, 152 (1924).

stance placed in the position AA or BB. The scattered rays passed out through a second mica window in the chamber C and thence to the ionization chamber D. The method consists of placing a certain thickness of aluminum absorber at P and noting the ionization current I_P, and then transferring this absorber to Q and noting the ionization current I_Q. If the scattered rays contain any modified rays, I_Q will be less than I_P and the ratio I_P/I_Q will be greater than unity. The value of I_P/I_Q then gives a measure of the percentage of the total scattered radiation which is modified. Knowing I_P/I_Q, the thickness transferred, the wave-length, and the angle of scattering, De Foe calculated this percentage by means of a formula developed by Jauncey and De Foe.[11] However, this formula is based on the assumption that the modified rays are all of the same wave-length whereas it has been pointed out by Jauncey[12] that the modified line has a width. Also, more recently, it has been

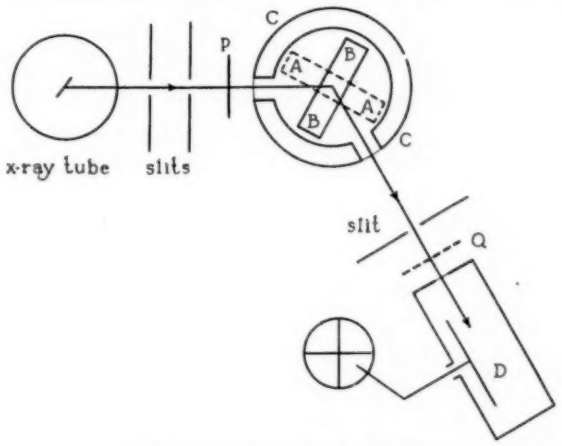

Fig. 1. Diagram of apparatus.

shown by Du Mond[13] and Davis and Purks[14] that the modified line has a structure. The formula of Jauncey and De Foe is therefore only an approximation and in this paper we shall content ourselves with finding the values of I_P/I_Q for given angles of scattering and given wave-lengths for three different temperatures of the scatterer and comparing the values for the different temperatures.

The heating chamber, or furnace consisted of an iron cup packed in asbestos. Imbedded in the asbestos was a heating coil of iron wire. The temperature inside the furnace was measured by placing a thermocouple just behind the scattering block. The furnace was heated for 60 minutes before readings were taken of the scattered x-rays. The temperature attained was 565°C.

The cooling chamber, or refrigerator, consisted of a copper cylinder of 2 in. diameter and 5.5 in. height. A cavity of 1.5 in. depth and 1.25 in. diameter

[10] O. K. DeFoe, Phys. Rev. **27,** 675 (1926).
[11] Jauncey and DeFoe, Phil. Mag. **1,** 714 (1926).
[12] G. E. M. Jauncey, Phys. Rev. **25,** 314 (1925).
[13] J. W. DuMond, Phys. Rev. **33,** 643 (1929).
[14] Davis and Purks, Phys. Rev. **33,** 1089 (1929).

was drilled in the top end of the cylinder. Windows at angles of 0°, 60° and 90° were drilled in the sides of the cup and a copper stopper screwed down a distance of 0.375 in. into the cup. The lower end of the copper cylinder dipped into liquid air which was contained in a Dewar flask. The upper part of the cylinder except for the windows was covered with felt. In order to prevent the deposition of frost on the mica windows, each mica window, which was on the outside of the felt, was surrounded by an iron wire which could be heated by means of an electric current. The temperature inside the cavity was determined by means of a thermocouple while the lower end of the cylinder was in the liquid air and the wires around the windows were being heated and was found to be −140°C.

Separate experiments were made with the furnace and with the refrigerator. In each case a set of readings was taken at room temperature (about 25°C), a second set at 565°C or −140°C according as the furnace or the refrigerator was used and a third set at room temperature again. The time between two successive sets was about an hour so as to give the scatterer time to come to a steady temperature. Each set of readings consisted of 8 readings of the ionization current with the aluminum absorber at P and 8 readings with the absorber at Q (see Fig. 1), the readings in the two positions being alternated. Since it is the ratio I_P/I_Q which is important and not the absolute values of I_P and I_Q it is seen that the only thing which can cause a difference in the ratio if the wave-length and angle of scattering are kept constant is the temperature. It was found to be unnecessary to correct for a leak because when the scatterer was removed from the furnace or refrigerator the ionization current was negligible.

In order to keep any characteristic radiation from entering the ionization chamber the thickness of the aluminum window of this chamber was 0.045 cm. The wave-length of the x-rays was determined as follows: The thickness of aluminum which was transferred from P to Q was placed at P and the ionization current measured. Additional thickness of aluminum was placed at P until the ionization current was reduced to half value. From this additional thickness the average absorption coefficient was found and the average wave-length determined from Compton's tables.[15]

3. Experimental Results

The experimental results are shown in Table I. Average wave-lengths are shown in the third column and the thickness of aluminum transferred from the P position to the Q position of Fig. 1 is shown in the fifth column. In the sixth, seventh and eighth columns are shown the values of I_P/I_Q for the temperatures of −140°C, 25°C and 565°C respectively. In the fourth column are shown the fractions of the respective beams of x-rays which consist of modified rays. These values are calculated by Jauncey and De Foe's formula[11] from the mean of the two or three values of I_P/I_Q. As pointed out previously, however, the formula is only approximately correct. These values are given so as to give some idea of the proportion of modified rays. In some cases our values of the proportion agree with the values given in De Foe's paper while in others there is considerable disagreement. We believe, however, that, due

[15] A. H. Compton, X-Rays and Electrons, p. 184.

TABLE I. *Values of I_P/I_Q at different temperatures.*

Substance	Scattering angle	λ A	Proportion modified rays	d cm	I_P/I_Q −140°C	I_P/I_Q 25°C	I_P/I_Q 565°C
Carbon (graphite)	60°	0.35	0.86	0.334	1.050	1.052	1.049
		.42	.77	.334	—	1.070	1.073
		.48	.74	.334	1.091	1.092	—
		.58	.63	.083	1.027	1.023	1.022
	75°	.46	.72	.334	—	1.121	1.119
		.58	.71	.166	—	1.086	1.084
		.62	.64	.083		1.044	1.048
	90°	.49	.83	.334	1.197	1.200	1.195
		.52	.77	.334	1.222	1.218	—
		.58	.76	.334	1.065	1.064	—
		.58	.76	.166	—	1.128	1.129
		.62	.76	.166	—	1.157	1.159
Aluminum	90°	.32	.58	.334	1.057	1.058	1.056
		.36	.55	.334	1.067	1.066	—
		.41	.52	.334	1.082	1.080	1.083
	130°	.37	.73	.334	—	1.159	1.157
		.45	.63	.334	—	1.198	1.202
		.50	.62	.083	—	1.069	1.064
Copper	90°	.33	.64	.334	1.072	1.066	1.064
		.36	.57	.334	1.070	1.070	1.066
		.42	.54	.334	1.095	1.093	1.097
	130°	.30	.64	.334	—	1.110	1.104
		.41	.60	.334	—	1.147	1.144

to our steady source of voltage, our values are more reliable than De Foe's values. It is necessary that the proportion be less than unity. We have obtained several values of I_P/I_Q for the case where all of the rays were of the modified type. No change of I_P/I_Q with change of temperature was observed. These values, however, are not recorded because no change of I_P/I_Q should be expected.

4. DISCUSSION

If the values in the last three columns of Table I are examined it will be seen that these values change very little with the temperature. Such changes as are shown are mostly within the probable error which was found to be about 0.004. If the values of I_P/I_Q for carbon are examined it will be seen that, comparing the values in the sixth with those in the seventh column and also the values in the seventh with those in the eighth column of Table I, there are seven small increases and eight small decreases with increase of temperature. For aluminum there are three increases and five decreases with increase of temperature. Hence it may be concluded that there is no change in the ratio of modified and unmodified scattering for a temperature range of −140°C to 565°C.

In the case of copper, there may be a slight decrease of I_P/I_Q with rise of temperature as there is only one increase, one no change and six decreases with rise of temperature. Even in the case of copper, however, the differences are about the size of the probable error and so there may be no effect due to

temperature. At the temperature of 565° the copper becomes coated with a scale of oxide and this may explain the preponderance of decreases because at the cold temperatures the scattering is done by copper whereas at the high temperature the scattering is partially done by copper oxide. It may, therefore, be safely concluded that the copper shows no change in the ratio of modified to unmodified scattering for the above temperature range.

The characteristic temperatures[16] for carbon (graphite), aluminum and copper as calculated from their densities and compressibilities are 1600°K, 396°K, and 309°K respectively. According to Debye,[1] the intensity of the x-rays diffusely scattered by a crystal is proportional to $(1-e^{-M})$ where M is a function of the temperature of the crystal, the characteristic temperature of the crystal and other quantities. If zero-point energy is assumed the function M is different from the case where no zero-point energy is assumed. The values of $1-e^{-M}$ have been calculated and are shown in Table II.

TABLE II. *Diffuse scattering from crystals.*

Substance	Scattering angle	Wave-length	$1-e^{-M}$					
			No zero-point energy			Zero-point energy		
		A	−140°C	25°C	565°C	−140°C	25°C	565°C
Carbon (graphite)	60°	0.32	0.017	0.079	0.375	0.323	0.362	0.564
		.58	.005	.025	.131	.113	.131	.221
	75°	.46	.012	.057	.236	.244	.274	.375
		.62	.006	.032	.173	.131	.156	.281
	90°	.48	.014	.069	.343	.274	.323	.523
		.62	.009	.043	.221	.189	.213	.356
Aluminum	90°	.32	.573	.939	1.000	.883	.983	1.000
		.41	.405	.817	.997	.727	.918	.998
	130°	.37	.632	.966	1.000	.928	.993	1.000
		.50	.435	.849	.998	.763	.936	1.000
Copper	90°	.32	.498	.866	1.000	.753	.939	1.000
		.43	.316	.686	.980	.537	.788	.986
	130°	.30	.725	.980	1.000	.925	.995	1.000
		.41	.498	.871	1.000	.753	.935	1.000

It is the opinion of the authors that the unmodified x-rays should be made up at least partially of the diffuse crystal scattering as predicted by Debye. If this is the case then the values of $(1-e^{-M})$ show that there should be a large variation in this diffuse crystal scattering with the temperature when there is no zero-point energy and a smaller but still considerable variation when there is zero-point energy. We should, therefore, expect to find a considerable variation of the ratio of the intensities of the modified and unmodified rays in the temperature range of our experiments. Our experiments, however, show no detectable variation and we are led to conclude that the diffuse scattering from crystals does not obey the formula developed by Debye.

[16] See P. Debye, Ann. d. Physik **43**, 49 (1914) and L. B. Loeb, Kinetic Theory of Gases, p. 385.

THE SECOND SPARK SPECTRUM OF LEAD
Pb III

By Stanley Smith
University of Alberta

(Received February 25, 1929)

Abstract

Some additional multiplets arising from combinations between triplet terms of Pb III have been found. These are $6^3P_{0,1,2}-8^3S_1$, $6^3P_{0,1,2}-7^3D_{1,2,3}$, $7^3P_{0,1,2}-7^3D_{1,2,3}$ and $6^3P_{0,1,2}-pp^3P_1$. Twenty-one lines arising from combinations between singlet terms and intercombinations between singlet and triplet terms have been identified. Of particular interest is the pp^1D_2 term which is found in combination with $6^3P_{1,2}$, 6^1P_1, $6^3F_{2,3}$ and 6^1F_3. Seven newly found lines of Tl II are also given, which correspond to some of the Pb III combinations classified in this paper.

THE spectrum of Pb III, being similar to that of Hg I and of Tl II, is derived from triplet and singlet terms. The most important terms to be expected are listed in Table I. In the first column the states, with the total quantum numbers, of the two valence electrons, are given, and the second column contains the resultant terms expressed in a notation which is used throughout this paper.

Table I.

State of Electrons	Terms		State of Electrons	Terms		
$6s6s$		6^1S_0	$6p6p$	$pp^3P_{0,1,2}$	pp^1D_2	pp^1S_0
$6s6p$	$6^3P_{0,1,2}$	6^1P_1	$6s7s$	7^3S_1	7^1S_0	
$6s6d$	$6^3D_{1,2,3}$	6^1D_2	$6s7p$	$7^3P_{0,1,2}$	7^1P_1	
$6s5f$	$5^3F_{2,3,4}$	5^1F_3	$6s7d$	$7^3D_{1,2,3}$	7^1D_2	

Experimental

Spectrograms have been taken of the spark spectrum of lead in hydrogen at a pressure of about 50 cm of mercury with an auxiliary spark gap in air in series with the main spark. By increasing the length of the auxiliary spark gap the lines belonging to the higher stages of ionization are progressively enhanced. The spark gap was arranged to be parallel to the slit of a Hilger one meter interchangeable spectrograph, employing both glass and quartz trains, so that the condensing lens of the spectrograph projected on to the slit images of the tips of the electrodes. The enhanced lines appear first at the electrode tips and gradually extend across the gap as the excitation voltage is increased by lengthening the auxiliary spark gap. Self induction was also inserted in the circuit and increased until only the arc lines appeared. Spectrograms were also obtained using as source the interrupted arc in air. Alternating voltages up to 1500 volts were applied to the electrodes, which were shunted by a condenser of capacity about 2 microfarads. On increasing

the applied voltage, the lines arising from the higher states of ionization of the lead atom appear or become stronger relative to those belonging to lower states. By these methods the lines could be sorted out into groups belonging to the various stages of ionization. Other data used in this investigation were wave-length measures of the vacuum spark spectrum of lead for the Schumann region made by Dr. R. J. Lang by means of a two meter grating, and measures[1] in the region above 2200 made by the writer with a two meter grating on a Rowland mounting.

Combinations of Triplet Terms

A preliminary account[2] of some of the triplet term multiplets has been given by the writer. On referring to a previously published paper[3] by K. R. Rao, A. L. Narayan, and A. S. Rao, which the writer has only recently been able to procure, it was found that the results in the two papers are in agreement for the $6^3P_{0,1,2}$—$6^3D_{1,2,3}$ and $6^3D_{1,2,3}$—$6^3F_{2,3,4}$ groups but differ for the $6^3P_{0,1,2}$—7^3S_1 triplet. In spite of the abnormal intensity relations between the lines chosen by Rao for this triplet—the intensities are given as 2, 4, 2 by Carroll and appear on Lang's plates as 9, 15, 12— it is quite certain that Rao's identification is the correct one. The writer has now found the $6^3P_{0,1,2}$—8^3S_1, $6^3P_{0,1,2}$—$7^3D_{1,2,3}$ and $7^3P_{1,2,3}$—$7^3D_{1,2,3}$ groups which afford ample evidence for the validity of the scheme of triplet term combinations. This scheme is given in Table II. For the sake of completeness the lines previously identified are included. There is still some uncertainty with regard to the $6^3P_{0,1,2}$—$pp^3P_{0,1,2}$ combinations. It seems, however, probable that λλ 1052, 1098 and 1308 constitute the $6^3P_{0,1,2}$—pp^3P_1 triplet, as this assignment would make the wave numbers of 6^3P_1—pp^3P_1 for Hg I, Tl II[4] and Pb III follow very closely the irregular doublet law (See Table V). It might be pointed out that λλ3909, 5857 have been classified as belonging to Pb II by Gieseler.[5]

Singlet Combinations and Intercombinations between Singlet and Triplet terms

On turning to the singlet term combinations the evidence for the validity of the choices made is not so conclusive. A distinctive feature of the spectra of Hg I and Tl II[4,6] is the appearance of strong lines due to intercombinations between singlet and triplet terms. The separations between the various triplet terms already found may therefore be expected to furnish some clue which will be of assistance in identifying these lines. Using the irregular doublet law and extrapolating from the known $6^1S_0-6^1P_1$ and $6^1S_0-6^3P_1$ combinations of Hg I and Tl II the lines λλ 1048, 1553, which are strong in the vacuum spark of lead, are suggested as the corresponding lines for Pb III.

[1] S. Smith, Trans. Roy. Soc. Canada **22**, 331 (1928).
[2] S. Smith, Proc. Nat. Acad. Sci. **14**, 878 (1928).
[3] K. R. Rao, A. L. Narayan, A. S. Rao, Indian Jour. Phys. **2**, 467 (1928).
[4] S. Smith, Proc. Nat. Acad. Sci. **14**, 951 (1928).
[5] Gieseler, Zeits. f. Physik **42**, 276 (1927).
[6] J. C. McLennan, A. B. McLay and M. F. Crawford, Trans. Roy. Soc. Canada **22**, 241 (1928).

TABLE II. *Triplet term combinations of Pb III.*

	6^3P_0		6^3P_1		6^3P_2
6^3D_1	†1030.44 (15) 97046	3991	†1074.63 (15) 93055 477	14597	†1274.56 (10) 78458 482
6^3D_2			†1069.15 (20) 93532	14592	†1266.79 (15) 78940 1032
6^3D_3					†1250.43 (20) 79972
7^3S_1	*1114.99 (9) 89687	3993	*1166.94 (15) 85694	14599	*1406.57 (12) 71095
8^3S_1	727.32 (0) 137491	3994	749.08 (3) 133497	14587	840.97 (4) 118910
7^3D_1	709.24 (3) 140996	3993	729.91 (0) 137003 198	14599	816.97 (0) 122404 220
7^3D_2			728.86 (4) 137201	14577	815.50 (2) 122624 444
7^3D_3					812.56 (5) 123068
pp^3P_1	1052.23 (7) 95036	3994	1098.39 (10) 91042	14595	1308.10 (15) 76447
	7^3P_0		7^3P_1		7^3P_2
7^3S_1	*4798.52 (4) 20834.0	164.0	*4761.03 (8) 20998.0	4941.5	*3854.04 (10) 25939.5
8^3S_1	*3706.13 (2) 26974.7	164.2	*3728.83 (3) 26810.5	4941.2	*4571.35 (5) 21869.3
7^3D_1	3279.91 (2) 30479.9	163.9	3297.64 (4) 30316.0 198.5	4941.0	3939.77 (1) 25375.0 198.7
7^3D_2			3276.19 (7) 30514.5	4940.8	3909.17 (5) 25573.7 449.6
7^3D_3					3841.62 (7) 26023.3
	6^3D_1		6^3D_2		6^3D_3
5^3F_3			†3137.92 (10) 31859.0 502.9	1030.9	†3242.86 (5) 30828.1 502.1
5^3F_2	†3043.92 (10) 32842.8	480.9	†3089.16 (6) 32361.9	1031.7	3190.89 (0) 31330.2 140.8
5^3F_4					†3176.61 (10) 31471.0
7^3P_2			*5523.5 (5) 18099.7	1032.2	*5857.67 (6) 17067.5

† Lines identified by Rao, Narayan, Rao and Smith.
* Lines identified by Rao, Narayan and Rao.

These lead to a wave-number difference of 30953 for $6^3P_1-6^1P_1$. Predictions can now be made for the $6^1P_1-6^3D_{1,2}$ and $6^1P_1-7^3S_1$ combinations. Lines are found to appear very close to the predicted postitons, as is shown in Table III. If λλ 1142, 1371, which have the appropriate separation, are selected as $6^3P_{1,2}-6^1D_2$ then λ1768 would be $6^1P_1-6^1D_2$. The wave-number

TABLE III. *Singlet term combinations and intercombinations with triplet terms.*

Combination	λ	Int.	ν Observed	ν Predicted
$6^1S_0-6^1P_1$	1048.86	50	95341	
$6^1S_0-6^3P_1$	1553.09	10	64388	
$6^1P_1-6^3D_1$	1610.34	2	62099	62102
$6^1P_1-6^3D_2$	1597.96	2	62580	62579
$6^3P_1-6^1D_2$	1142.93	5	87494	
$6^3P_2-6^1D_2$	1371.80	6	72897	72899
$6^1P_1-6^1D_2$	1768.67	6	56540	56541
$6^1P_1-7^3S_1$	1826.86	2	54739	54741
$6^1D_2-5^3F_3$	2637.70	1	37900.5	37899
$6^1D_2-5^1F_3$	2562.27	10	39016.2	
$6^3D_2-5^1F_3$	3031.65	4	32975.8	32976
$6^3D_3-5^1F_3$	3129.63	0	31943.4	31944
$6^1D_2-7^3P_2$	4141.42	3	24139.5	24138
$6^1D_2-7^3P_1$	5207.15	3	19199.0	19197
$6^3P_1-pp^1D_2$	995.75	10	100427	
$6^1P_1-pp^1D_2$	1439.42	15	69472	69474
$6^3P_2-pp^1D_2$	1165.05	8	85833	85832
$pp^1D_2-5^1F_3$	3832.83	6	26083.0	26083
$pp^1D_2-5^3F_2$	4004.16	2	24967.0	24965
$pp^1D_2-5^3F_2$	3925.23	0	25469.0	25468
$pp^3P_1-5^3F_2$	2868.16	2	34855.4	34852

The wave-lengths below 2000A are in I.A. vac.
Those above 2000A are in I.A. air.

difference 6040 of $6^1D_2-6^3D_2$ can then be applied to predict the position of $6^1D_2-5^3F_3$ which is apparently the line λ2637. The strong line λ2562 appears to be $6^1D_2-5^1F_3$ as the 6040 separation of $6^1D_2-6^3D_2$ and the 1032 separation of $6^3D_2-6^3D_2$ lead to observed lines at λλ3031, 3129.

The group of strong lines λλ995, 1165, 1439 are of particular interest. They may be expressed as 6^3P_1-x, 6^3P_2-x and 6^1P_1-x. The only other terms with which x has been found to combine are 5^3F_2, 5^3F_3 and 5^1F_3. The obvious conclusion is that x is the pp^1D_2 term. According to the rules for the transitions between states of atoms with two valence electrons,[7] the pp^1D_2 term, which arises from a $6p$ $6p$ arrangement, can combine with terms arising from the following states:

(*a*)	$ns\cdot np$	$\Delta l_1=-1$	$\Delta l_2=0$
(*b*)	$np\cdot nd$	$\Delta l_1=0$	$\Delta l_2=1$
(*c*)	$ns\cdot nf$	$\Delta l_1=-1$	$\Delta l_2=2$
(*d*)	$nd\cdot nf$	$\Delta l_1=1$	$\Delta l_2=2$

Of all the terms which result from these configurations only those arising from (a) and (c) are known. The lowest of these are $6^3P_{0,1,2}$, 6^1P_1, $5^3F_{2,3,4}$ and

[7] W. Grotrian, Graphische Darstellung der Spektren p. 204, Springer, (1928).

5^1F_3. The selection rule for inner quantum numbers limits the terms with which pp^1D_2 can combine to $6^3P_{1,2}$, 6^1P_1,$5^3F_{2,3}$ and 5^1F_3. All these combinations have been found. The combinations $4^3P_{1,2}-pp^1D_2$ for Zn I have been given by Sawyer[8].

Of the classified lines recorded in Table III the identity of five has been assumed and the wave-numbers of the remaining sixteen have been predicted on the basis of these five identifications and of the triplet combination assignments of Table II.

In order to obtain the term values the difference 7^3S_1—8^3S_1 has been used in a Rydberg formula giving the approximate value 109400 for 7^3S_1. In the case of Hg I a similar calculation gives a value for 7^3S_1 which is one and a half percent larger than the true value. Assuming that a corresponding correction should be applied in the case of Pb III, the value of 7^3S_1 may be taken to be 107750. A similar process carried out on the $6^3D_1-7^3D_1$ difference gives a value 102325 for 6^3D_1. This would lead to a value 109700 for 7^3S_1. 108700, which is approximately the mean of these two values of 7^3S_1 has been used to obtain the term values given in Table IV. The ionization potential of the doubly ionized atom of lead is found to be 31.93 volts. The resonance potential is 7.95 volts.

TABLE IV. *Term Values of Pb III.*

Term	Value	Term	Value	Term	Value	Term	Value
6^1S_0	258778	6^1D_2	106896	7^3P_0	87866	5^1F_3	67880
6^3P_0	198383	pp^3P_1	103347	7^3P_1	87702	8^3S_1	60891
6^3P_1	194390	6^3D_1	101337	7^3P_2	82761	7^3D_1	57386
6^3P_2	179795	6^3D_2	100856	5^3F_2	68998	7^3D_2	57187
6^1P_1	163437	6^3D_3	99825	5^3F_3	68495	7^3D_3	56737
7^3S_1	(108700)	pp^1D_2	93963	5^3F_4	68354		

Since both 6^1D_2 and pp^1D_2 combine with the same P and F terms it is possible that the two term values in Table IV for 6^1D_2 and pp^1D_2 should be interchanged. The main argument in favor of the choice given here is that in the case of Mg I, Zn I, Cd I, Hg I and Tl II the $^1D_2$ term in each case is lower than the corresponding $^3D_1$ term. If 89108 were taken as 6^1D_2 then the 6^3D_1 term would be lower than this value by 7375. Also the assigned value of 89108 for pp^1D_2 is in reasonably good agreement with the expected relative values of the pp^3P_1 and pp^1D_2 terms.

The sequence of values of the wave-numbers of $6^3P_1-pp^3P_1$, $6^1S_0-6^1P_1$ and $6^1S_0-6^3P_1$ for mercury-like atoms is given in Table V.

TABLE V. *Irregular doublet law for mercury-like atoms.*

	$6^3P_1-pp^3P_1$	Difference	$6^1S_0-6^1P_1$	Difference	$6^1S_0-6^3P_1$	Difference
Hg I	54576	18365	54066	21590	39412	12981
Tl II	72941	18101	75656	19685	52393	11995
Pb III	91042		95341		64388	

[8] R. A. Sawyer, J.O.S.A. **13**, 432 (1926).

Note on the Spectrum of Tl II.

A search has been made in the spectrum of Tl II for the combinations of the pp^1D_2 term with the $6^3P_{1,2}$ and 6^1P_1 terms. These three combinations have been found, and are given in Table VI, together with some combinations additional to those already classified[4,6]. The $ppD5F$ combinations would be expected to lie far in the infra-red, the calculated wave-number of $5^1F_3 - pp^1D_2$ being 7447.

Table VI. *Some further lines of Tl II.*

Classification	λ	Intensity	ν
$6^3P_1 - pp^1D_2$	1308.52	2	76422
$6^3P_2 - pp^1D_2$	1490.50	5	67092
$6^1P_1 - pp^1D_2$	1881.22	6	53157
$6^1D_2 - 5^1F_3$	4737.07	30	21104.0
$6^1D_2 - 5^3F_3$	4770.88	1	20954.6
$6^3D_3 - 5^1F_3$	5040.69	0	19833.0
$6^3D_2 - 5^1F_3$	5143.7	0	19436

The line λ5143 is taken from MacQuarrie's wave-length measures[9] of the spectrum obtained from an electrodeless discharge in thallium vapor. λλ4770, 5041 and 5143 are given by MacQuarrie as Tl III lines. It should be mentioned that λ1490 had previously been classified by the writer as $6^3P_1 - pp^3P_0$.

The Principal Quantum Numbers Of The Lowest Fundamental Terms

The principal quantum numbers of the lowest S, P, D and F terms of the elements have been assigned on more or less theoretical grounds by Bohr and others. The conclusions arrived at are given in a clear and concise manner by Grotrian.[7] The lowest F terms of the zinc-like system and of the cadmium-like system are stated to have the principal quantum number 4 while 5 is given as the principal quantum number of the lowest F terms of mercury-like system. Combinations between the lowest ^3D terms, and terms which are generally supposed to be the lowest[3] F terms, have been identified for some of the atoms in the above mentioned systems by various investigators.

The wave-numbers of the $^3D_3 - {}^3F_4$ members are collected in Table VII.

If x is assigned the value 4, as is the usual practice, it is surprising to find that the wave-numbers do not follow the irregular doublet law. The generally accepted value of y is 4 and yet it will be observed that the wave-number differences are almost equal for the cadmium-like sequence, indicating that y should probably be given the value 5. It may be that the lowest ^3F terms for these atoms have yet to be found. In the case of the mercury-like system the wave-number differences suggest that z should be assigned the value 6. However, in the present paper the more generally accepted value 5 has been used.

[9] W. C. MacQuarrie, Trans. Roy. Soc. Canada 19, 57 (1925).

TABLE VII.

	$4^3D_3-x^3F_4$ Difference			$5^3D_3-y^3F_4$ Difference			$6^3D_3-z^3F_4$ Difference	
ZnI[10]	6060		Cd I[10]	6066		Hg I[10]	5815	
		17396			15286			13588
Ga II[11]	23456		In II[11,12]	21352		Tl II [3]	19403	
		24045			16251			12068
Ge III[13]	47501		Sn III[13]	37603		Pb III[2,3]	31471	

In conclusion I wish to thank Dr. Lang for the use of his list of wavelengths in the Schumann region and to acknowledge a grant from the National Research Council of Canada.

Note added July 3, 1929. Since the above paper was written I have been investigating the Schüler lamp discharge of thallium. The lines λλ5040 and 5143 classified above in Table VI as $6^3D_{2,3}-5^1F_3$ appear on the plates with intensities 3 and 1 respectively. The new measures are 5040.50A and 5142.84A and give a wave-number difference fo 4937 for $6^3D_2-6^3D_3$. There can now be no doubt that these lines belong to Tl II and the evidence in support of the classification in Table VI is further strengthened.

[10] A. Fowler, Series in Line Spectra, 1922.
[11] K. R. Rao, Proc. Phys. Soc. London **39**, 161 (1927).
[12] J. B. Green and R. A. Loring, Phys. Rev. **30**, 574 (1927).
[13] R. J. Lang, Proc. Nat. Acad. Sci. **14**, 32 (1928).

AN EXTENSION OF THE Cd I-LIKE ISOELECTRONIC SEQUENCE TO Sb IV AND Te V*

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ABSTRACT

Sn III.—New lines, in addition to those classified by Green and Loring, have been identified in this spectrum, in particular, second members of series.

Sb IV.—Lines have been identified arising from transitions $5s5p$ to $5s^2$; and from $5p^2$, $5s5d$, and $5s6s$ to $5s5p$. Some second members have also been found.

Te V.—The Cd I-like isoelectronic sequence has been extended through this element, by the classification of lines resulting from transitions between the same electronic configurations as for Sb IV.

THE spectra of tin, antimony and tellurium used in this report were photographed with a vacuum spectrograph, which has been previously described.[1] For this work a grating of speculum metal with about 15,000 lines to the inch, and a radius of curvature of 150 cm was used. The disper-

TABLE I. *Doubly ionized tin*, Sn, III.

λ	ν	Int.	Designation	Multiplet No.
*2665.60	37503.9	1	$5^3D_3-4^3F_3$	9
*2658.64	37602.0	10	$5^3D_3-4^3F_4$	9
*2646.18	37779.1	2	$5^3D_3-4^3F_3$	9
*2643.60	37816.0	6	$5^3D_3-4^3F_2$	9
*2631.87	37984.5	4	$5^3D_1-4^3F_2$	9
?2109.89	47395.8	1	$5^1P_1-5^3P_0'$	15
2070.68	48293.3	10	$5^1P_1-5^1D_2$	17
1991.68	50208.9	000	$5^1P_1-5^3P_1'$	15
1829.61	54656.5	000	$5^1P_1-5^3P_2'$	15
*1811.90	55191	20	$5^1S_0-5^3P_1$	7
*1674.47	59720	2	$5^1P_1-6^3S_1$	4
*1628.51	61406	3	$5^1P_1-5^3D_1$	6
*1623.13	61609	4	$5^1P_1-5^3D_2$	6
*1570.41	63677	12	$5^1P_1-5^1D_2$	5
1449.73	68978	25	$5^3P_2-5^1D_2$	16
*1410.68	70888	30	$5^3P_2-5^3P_1'$	3
1386.74	72112	20	$5^3P_1-5^3P_0'$	3
1369.71	73008	12	$5^3P_1-5^1D_2$	16
*1334.74	74921	30	$5^3P_1-5^3P_1'$	3
*1327.40	75335	30	$5^3P_2-5^3P_2'$	3
*1306.01	76569	15	$5^3P_0-5^3P_1'$	3
*1259.97	79367	20	$5^3P_1-5^3P_2'$	3
*1251.43	79908	50	$5^1S_0-5^1P_1$	8
*1243.70	80405	20	$5^3P_2-6^3S_1$	1
*1218.23	82086	3	$5^3P_2-5^3D_1$	2
*1215.14	82295	15	$5^3P_2-5^3D_2$	2
*1210.55	82607	30	$5^3P_2-5^3D_3$	2
*1184.33	84436	20	$5^3P_1-6^3S_1$	1
*1161.62	86087	20	$5^3P_0-6^3S_1$	1
*1161.09	86126	20	$5^3P_1-5^3D_1$	2
*1158.37	86328	20	$5^3P_1-5^3D_2$	2
*1139.35	87769	20	$5^3P_0-5^3D_1$	2
910.92	109779	4	$5^1P_1-6^1D_2$	12
784.68	127440	6	$5^3P_2-7^3S_1$	10
776.58	128770	00	$5^3P_2-6^3D_2$	11
775.79	128901	5	$5^3P_2-6^3D_3$	11
760.54	131486	3	$5^3P_1-7^3S_1$	10
753.47	132719	0	$5^3P_1-6^3D_1$	11
753.01	132800	4	$5^3P_1-6^3D_2$	11
744.24	134365	0	$5^3P_0-6^3D_1$	11
*624.00	160256	00	$5^1S_0-6^3P_1$	13
*614.60	162707	3	$5^1S_0-6^1P_1$	14

* Wave-lengths and classification by Green and Loring.

sion obtained was about 11.3Å per mm. In general, four exposures were taken on each plate; (1) a short exposure from a vacuum spark of the metal being studied, (2) a long exposure of the same element, (3) a longer exposure

* A brief report describing some of the results presented in this paper was made at the Pomona Meeting of the American Physical Society, June, 1928.

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[1] Gibbs and White, Phys. Rev. 31, 776 (1928).

of the metal using an inductance in series with the spark, and (4) the spectrum given by aluminum, for standards. In the case of tellurium the metal was consumed so rapidly that it was found necessary to use one of its alloys. An alloy of aluminum and tellurium proved to be very satisfactory, and little difficulty was encountered in distinguishing the lines contributed by each of the metals in the alloy.

TABLE II. *Triply ionized antimony*, Sb IV.

λ	ν	Int.	Designation	Multiplet No.	λ	ν	Int.	Designation	Multiplet No.
*2113.14	47323	3	$5^3D_3-4^3F_3$	9	†940.28	106351	6	$5^3P_1-5^3D_1$	2
*2106.00	47483	10	$5^3D_2-4^3F_3$	9	†937.17	106704	15	$5^3P_2-5^3D_2$	2
*2092.26	47795	2	$5^3D_2-4^3F_2$	9	†932.32	107259	25	$5^3P_2-5^3D_3$	2
*2088.53	47880	10	$5^3D_3-4^3F_4$	9	†891.17	112212	20	$5^3P_1-5^3D_1$	2
*2076.99	48146	5	$5^3D_1-4^3F_2$	9	†888.40	112562	25	$5^3P_1-5^3D_2$	2
1666.93	59991	15	$5^1P_1-5^1D_2$	17	†873.56	114474	20	$5^3P_0-5^3D_1$	2
1654.93	60426	00	$5^1P_1-5^3P_1'$	15	†861.60	116063	25	$5^3P_2-6^3S_1$	1
1499.24	66700	25	$5^1S_0-5^3P_1$	7	†820.21	121920	25	$5^3P_1-6^3S_1$	1
?1480.05	67565	15	$5^1P_1-5^3P_2'$	15	†805.24	124187	15	$5^3P_0-6^3S_1$	1
?1205.18	82975	15	$5^1P_1-5^3D_1$	6					
1200.32	83311	00	$5^1P_1-5^3D_2'$	6	626.54	159606	2	$5^1P_1-6^1D_2$	12
1199.10	83396	25	$5^3P_2-5^1D_2'$	16	548.68	182255	0	$5^3P_2-6^3D_3$	11
†1192.92	83828	25	$5^3P_2-5^3P_1'$	3	547.90	182515	4	$5^3P_2-6^3D_2$	11
1171.38	85370	20	$5^3P_1-5^3P_0'$	3	539.90	185219	6	$5^3P_2-7^3S_1$	10
?1151.49	86844	40	$5^1P_1-5^1D_2'$	5	532.04	187956	00	$5^3P_1-6^3D_1$	11
1120.38	89255	8	$5^3P_1-5^1D_2'$	16	531.54	188132	1	$5^3P_1-6^3D_2$	11
†1115.05	89682	25	$5^3P_1-5^3P_1'$	3	523.38	191064	3	$5^3P_1-7^3S_1$	10
1099.33	90964	30	$5^3P_2-5^3P_2'$	3	517.24	193334	00	$5^3P_0-7^3S_1$	10
†1087.64	91942	8	$5^3P_0-5^3P_1'$	3	463.47	215763	0	$5^1S_0-6^1P_1$	13
†1042.21	95950	75	$5^1S_0-5^1P_1$	8	456.50	219058	1	$5^1S_0-6^1P_1$	14
1032.88	96817	30	$5^3P_1-5^3P_2'$	3					

* Identifications by Green and Lang. † Independent identifications by Green and Lang and by the authors.

The spectra obtained when using an inductance in series with the spark proved to be of considerable value. Lines belonging to various states of ionization were differently affected in intensity and form. In general the addition of series inductance gave lines which were relatively stronger in intensity for lower states of ionization and weaker for higher states. It thus became possible to ascribe a fairly definite type of line to a particular state of ionization.

TABLE III. *Quadruply ionized tellurium*, Te V.

λ	ν	Int.	Designation	Multiplet No.	λ	ν	Int.	Designation	Multiplet No.
1549.28	64546	2	$5^1P_1-5^3P_0'$	15	895.20	111707	60	$5^1S_0-5^1P_1$	8
1406.56	71095	10	$5^1P_1-5^1D_2$	17	872.81	114572	4	$5^3P_1-5^3P_0'$	3
1281.67	78023	25	$5^1S_0-5^3P_1'$	7	771.55	129609	000	$5^3P_0-5^3D_1$	2
1236.31	80886	3	$5^1P_1-5^3P_0'$	15	768.43	130135	4	$5^3P_2-5^3D_3$	2
1037.08	96424	8	$5^3P_2-5^3P_1'$	3	763.41	130991	15	$5^3P_2-5^3D_2$	2
1033.04	96802	12	$5^3P_2-5^1D_2$	16	726.82	137586	6	$5^3P_1-5^3D_1$	2
1018.07	98225	10	$5^3P_1-5^3P_2'$	3	724.04	138114	10	$5^3P_1-5^3D_2$	2
957.89	104396	5	$5^3P_1-5^3P_1'$	3	711.73	140503	5	$5^3P_0-5^3D_1$	2
954.47	104770	10	$5^3P_1-5^1D_2$	16	645.85	154835	2	$5^3P_2-6^3S_1$	1
938.14	106594	7	$5^3P_2-5^3P_2'$	3	614.20	162813	0	$5^3P_1-6^3S_1$	1
931.90	107308	4	$5^3P_0-5^3P_1'$	3	603.40	165728	000	$5^3P_0-6^3S_1$	1
?910.86	109786	8	$5^1P_1-5^1D_2$	5					

The neutral unexcited atoms of antimony and tellurium contain five ($5s^25p^3$) and six ($5s^25p^4$) valence electrons respectively. The removal of three electrons ($5p^3$) from antimony and four ($5p^4$) from tellurium places these elements as the fourth and fifth members in the sequence of isoelectronic systems starting with cadmium: Cd I, In II, Sn III, Sb IV, Te V. Guided by

transitions already established for cadmium,[2] indium,[3] and tin[4] from $^3P_{012}$, $^1P_1(5s5p)$ to $^1S_0(5s^2)$ and from $^3S_1$, $^1S_0(5s6s)$; $^3D_{123}$, $^1D_2(5s5d)$; and $^3P'_{012}$, $^1S_0$, $^1D_2(5p^2)$ to $^3P_{012}$, $^1P_1(5s5p)$, it has been possible by an almost linear extrapolation of the classified lines to locate many of the corresponding lines in the spectra of Sb IV and Te V. This type of extrapolation is illustrated in Fig. 1, where relative intensities and increase of term separations may also be noted.

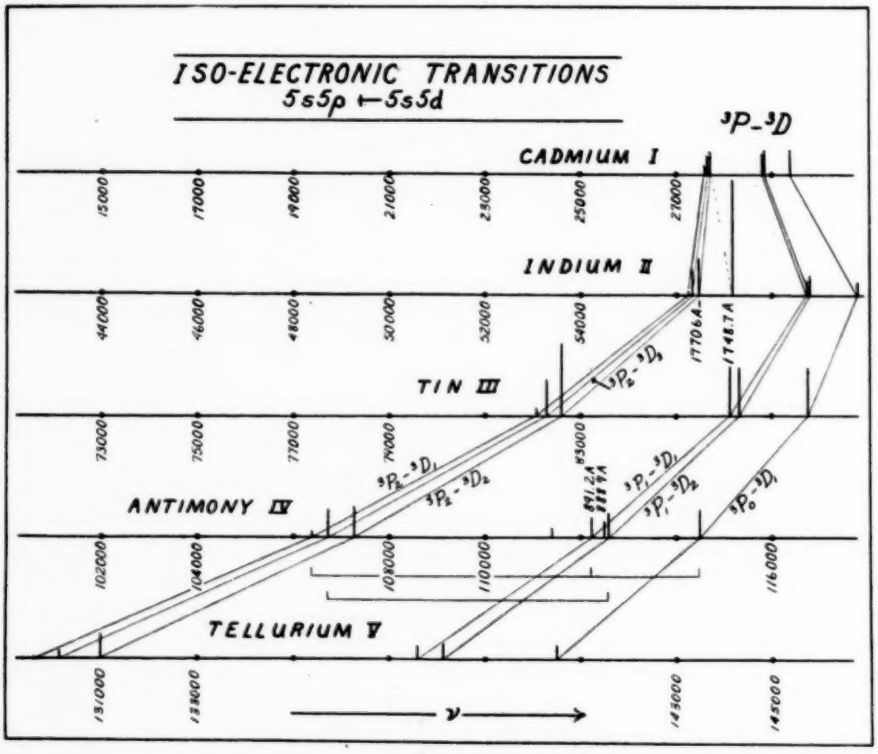

Fig. 1.

Lang[3] selected for the transition $^3P_2 - {}^3D_3$ in In II the very intense line at $\nu = 57185$, $\lambda = 1748.71$A, although he had previously used this same line for the transition $^2S_1 - {}^2P_1$ in In III.[5] (Fig. 1.) The less intense line at $\nu = 56475$, $\lambda = 1770.6$A, reported by Carroll,[6] appears to fit into the frequency diagram much better than the one connected by the dotted line at 57185. In the case of Sb V Lang[5] has used for the transition $^2P_2(5p) - {}^2D_3(5d)$ the line at 891.17A, (Fig. 1). This line, however, fits well into the scheme for Sb IV. Moreover, the exposure showing the effect of inductance, reproduced in Fig. 1 B of the

[2] Fowler, Report on Series in Line Spectra, 1922.
[3] Lang, Phys. Rev. 30, 762 (1927).
[4] Green and Loring, Phys. Rev. 30, 574 (1927).
[5] Lang, Proc. Nat. Acad. Sci. 13, 341 (1927).
[6] Carroll, Phil. Trans. Roy. Soc. A225, 408 (1926).

succeeding article, indicates that this line is of the same type as others belonging to Sb IV. Possibly the line at 888.97A may be used for the above transition in Sb V instead of the line at 891.17A. At least the character of the former line, when photographed with series inductance, is similar to that of other lines belonging to the spectrum of quadruply ionized antimony. By thus identifying the line 891.17A as arising from the transition $^3P_1(5s5p) - {}^3D_1(5s5d)$ in the spectrum of Sb IV, not only does the frequency of this transition pro-

TABLE IV. *Term values.*

Configuration (Limit)	Term	Term Values Sn III	Sb IV	Te V	Multiplet Number
$5s^2$ $5s$	$^1S_0$	247302	356156	486244	7, 8, 13, 14
$5s5p$	$^3P_0$	193758	291721	411135	1, 2, 3, 10, 11
$5s$	$^3P_1$	192111	289456	408221	1, 2, 3, 7, 10, 11, 16
	$^3P_2$	188077	283596	400247	1, 2, 3, 10, 11, 16
	$^1P_1$	167394	260204	374537	4, 5, 6, 8, 12, 15, 17
$5p^2$	$^3P_0'$	120000	204086	309996	3, 15
$5p$	$^1D_2$	119106	200200	303447	16, 17
	$^3P_1'$	117190	199774	303825	3, 15
	$^3P_2'$	112741	192639	293652	3, 15
	$^1S_0$				
$5s6s$	$^3S_1$	107672	167534	245407	1, 4
$5s$	$^1S_0$				
$5s5d$	$^3D_1$	105989	177244	270632	2, 6, 9
$5s$	$^3D_2$	105783	176894	270107	2, 6, 9
	$^3D_3$	105470	176337	269255	2, 9
	$^1D_2$	103717	173360	264751	5
$5s6p$	$^3P_0$				
$5s$	$^3P_1$	87097	140393		13
	$^3P_2$				
	$^1P_1$	84581	137098		14
$5s4f$	$^3F_2$	68004	129099		9
$5s$	$^3F_3$	67967	129014		9
	$^3F_4$	67868	128854		9
	$^1F_3$				
$5s7s$	$^3S_1$	60625	98385		10
$5s$	$^1S_0$				
$5s6d$	$^3D_1$	59394	101500		11
$5s$	$^3D_2$	59311	101330		11
	$^3D_3$	59175	101081		11
	$^1D_2$	57615	100585		12

gress more smoothly through the elements of this isoelectronic system but the increase in the $^3D_{1,2}$ separation is much more regular.

Second members of some of the series in the spectra of Sn III and Sb IV have been identified. Their classification has made possible the determination of some of the approximate term values for these elements directly, while radiated frequencies enable us to estimate other term values. The plate for tin gives evidence of very faint lines in the vicinity of 665A, where one would

expect third members of some of these same series to appear. Since these lines could not be accurately measured they have not been included in this report. Our plates on tellurium did not bring out the second members of any of the series.

The lines in cadmium at 2239.9A, 2267.5A, and 2329.3A, taken from Fowler's[2] list of unclassified lines in the arc spectrum of that element, have been identified as $^3P_{012}-{}^3P_1'$.

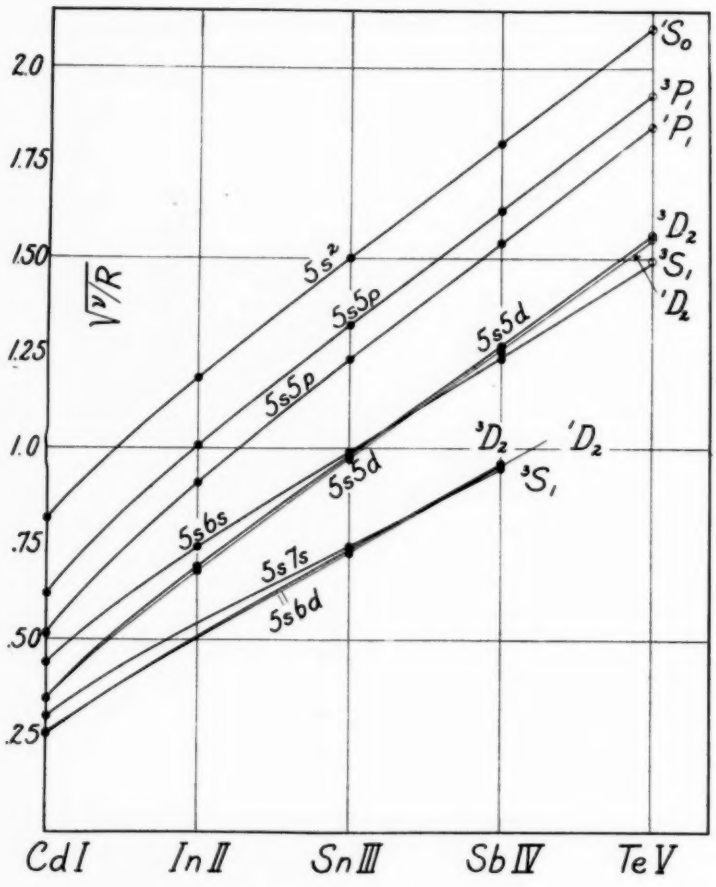

Fig. 2. Moseley diagram.

In the Moseley diagram, Fig. 2, the points for tellurium have been obtained merely by an extension of the curves given by the previous four elements. Evaluation of these points has given the term values for tellurium as recorded in Table IV.

The issue of Nature for August 18, 1928 contains a brief report by Green and Lang on the spectrum of trebly ionized antimony. A further report by them appeared in the September issue of the Proceedings of the National Academy of Sciences. At that time we had not definitely chosen the 5^3D-4^3F

multiplet. However, further investigation has shown these to be the only characteristic lines in the general region where one should expect to find this multiplet. For the sake of completeness, we have, therefore, included these lines in this report, as well as others chosen both by Green and Lang[7] and by ourselves. Their choice of three lines in the $5^3P-5^3P'$ multiplet, at 1145.86A, 1120.43A and 1051.33A, of $5^1S_0-5^3P_1$ at 1513.3A, of $5^1P_1-6^3S_0$ at 1086.5A and of $5^1P_1-5^3D_1$ at 1214.8A differs from ours. Aided by our observations of the influence of inductance on the quality of lines we may say that with the exception of the line at 1120.4A, the lines enumerated do not appear to belong to that class which is typical of Sb IV.

TABLE V. *Term separations.*

	$5s5p$			$(5p)^2$			$5s5d$			$5s6d$			$5s4f$		
	$^3P_2$	$^3P_1$	$^3P_0$	$^3P_2'$	$^3P_1'$	$^3P_0'$	$^3D_3$	$^3D_2$	$^3D_1$	$^3D_3$	$^3D_2$	$^3D_1$	$^3F_4$	$^3F_3$	$^3F_2$
Sn III	4034	1647		4446	2809		313	206		131	81		99	37	
Sb IV	5860	2265		7135	4312		557	350		260	176		160	85	
Te V	7977	2914		10173	6171		856	527		—	—		—	—	

The line at 1120.43A has been identified as one of a pair of lines belonging to the transition $5^3P_{12}-5^1D_2$. Both these lines are identical in character with those of the $^3P-^3P'$ multiplet and appear in the same region with them. In Sn III and Te V similar pairs of lines are found. A corresponding identification in Sn III makes use of the line at 1369.76A, previously identified[4] as $^3P_1-^3P_0'$. However, this line is unquestionably associated with the $^3P_{12}$ interval, and in its stead we have chosen the line at 1386.76A for the transition $^3P_1-^3P_0'$.

In the accompanying tables some lines have been marked as questionable. This indicates either that the intensity appears abnormal, or that there is some doubt about the type of line produced by the inductance. In some cases these irregularities may merely mean the presence of two lines of different types or intensity, which the apparatus available has failed to resolve.

[7] Green and Lang, Proc. Nat. Acad. Sci. **14**, 707 (1928).

THE USE OF SERIES INDUCTANCE IN VACUUM SPARK SPECTRA*

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(Received June 15, 1929)

Abstract

Examples are given which illustrate the effect of series inductance on the intensity and form of lines in the vacuum spark spectra of antimony and tin and its use as an aid in the identification of the lines in the spectra of these two elements.

WHILE endeavoring to solve certain difficulties which arose in the identification of lines belonging to the spectrum of Sb IV it became necessary to have other criteria available than those which the ordinary methods of classification afford. Fowler[1] has utilized to some extent, inductance in series with ordinary sparks in air and refers to its usefulness in the case of spark spectra in vacuo. By investigating the effect of varying inductance on the spectra of several elements, Kimura and Nakamura[2] have been able to sort out lines in the visible and near ultra-violet regions belonging to various stages of ionization of the atom. Rao[3] has also made use of the effect of varying the inductance in the secondary circuit, in his study of the spectra of some of the elements. The authors have employed this same method in their study of the vacuum spark spectra of tin, antimony and tellurium in the region below 2600A.

By making several exposures on the same plate, and by making a careful study of the relative quality of the lines, it has been possible to sort the lines into groups representing five different stages of ionization. In general the use of inductance serves to strengthen lines arising from lower states of ionization and to weaken those from higher states. Although some detail has been lost in enlarging and reproducing portions of the original plates, nevertheless, the plates included in this report serve to bring out the essential differences in the spectra produced with and without inductance. Lines belonging to various stages of ionization are so indicated in the figures. In all the exposures reproduced in this paper, which are labelled "with series inductance," a coil 16.5 cm in length and 7.8 cm in diameter and consisting of a single layer of 71 turns of No. 18 copper wire was inserted in series with the spark gaps and condenser.

In identifying the lines belonging to Sb IV this method proved to be particularly useful. Fig. 1 B indicates the line at λ891.17A which Lang[4] had previously used for Sb V. As is apparent from the figure, this line, as well as

* The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[1] Fowler, Phil. Trans. Roy. Soc. **A225**, 1 (1925).
[2] Kimura and Nakamura, Jap. Jour. Physics **3**, 200 (1924).
[3] Rao, Phys. Soc. London Proc. **39**, 150, 161, 408 (1926–1927).
[4] Lang, Proc. Nat. Acad. Sci. **13**, 341 (1927).

others belonging to Sb IV, is weakened in the inductance spectrum,while certain other strong lines, presumably due to Sb V are entirely cut out by the self-inductance One seems justified then in definitely assigning this line to trebly ionized antimony.[5]

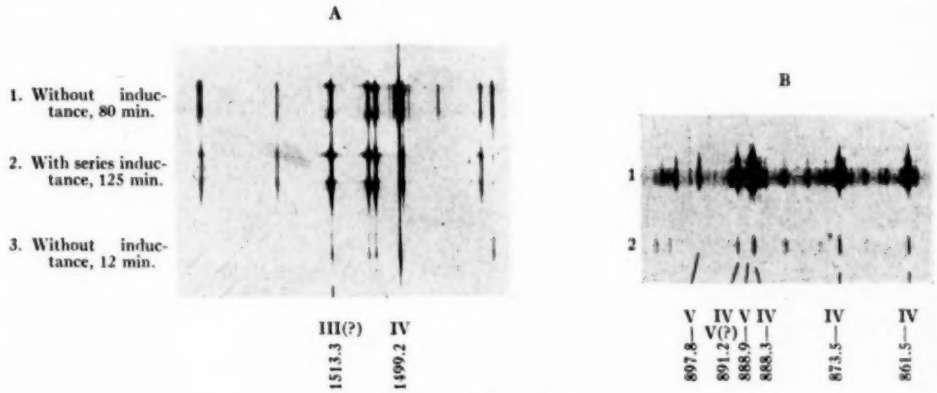

Fig. 1. Antimony

Fig. 2 shows some of the characteristic lines of Sb IV belonging to the $^3P-{}^3P'$ multiplet. The lines at λ1171.38A, 1099.33A and 1032.88A, which show the characteristic effects of self-induction for most of those lines already chosen for Sb IV, have been used in our selection of lines belonging to this multiplet. Those lines at λ1145.86A, 1120.43A and 1051.33A are the corresponding ones chosen by Green and Lang.[6] Observations indicate that of these

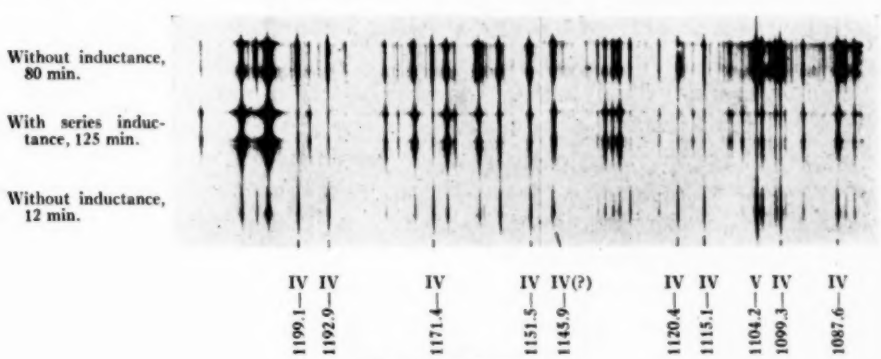
Without inductance, 80 min.
With series inductance, 125 min.
Without inductance, 12 min.
IV IV IV IV IV(?) IV IV V IV IV
1199.1 1192.9 1171.4 1151.5 1145.9 1120.4 1115.1 1104.2 1099.3 1087.6

Fig. 2. Antimony

lines the first and last do not belong to Sb IV. We have identified the characteristic line at 1120.38A as $^3P_1-{}^1D_2$, as it is definitely associated with another similar line at 1199.1A, ($^3P_2-{}^1D_2$). The line chosen by them at 1513.34A as $^1S_0-{}^3P_1$ (Sb IV) appears to belong either to Sb II or Sb III, (Fig. 1A). The same figure shows the line at 1499.2A which is our choice for the same transition.

Fig. 3 serves nicely to bring out the different classes of lines for tin in various stages of ionization. The lines belonging to Sn II are increased considerably in intensity by the use of inductance while those of Sn III are not strengthened as much. Lines identified as Sn IV are decreased slightly

[5] Preceding paper.

[6] Green and Lang, Proc. Nat. Acad. Sci. **14**, 707 (1928).

in intensity, while those classified as Sn V appear considerably decreased in intensity, with only the ends of the lines evident. The lines in the vicinity of 1131A have been chosen by Lang[4] as possibly belonging to Sn IV. Evidence here indicates such a classification as incorrect. Gibbs and White[7] have classified the line at 1189.98A as belonging to Sn V. Figure 3 indicates that this line is incorrectly classified as belonging to quadruply ionized tin, unless there is present at the same wave-length a line belonging to a lower state of ionization, thus causing the presence of a stronger line in the inductance spectrum

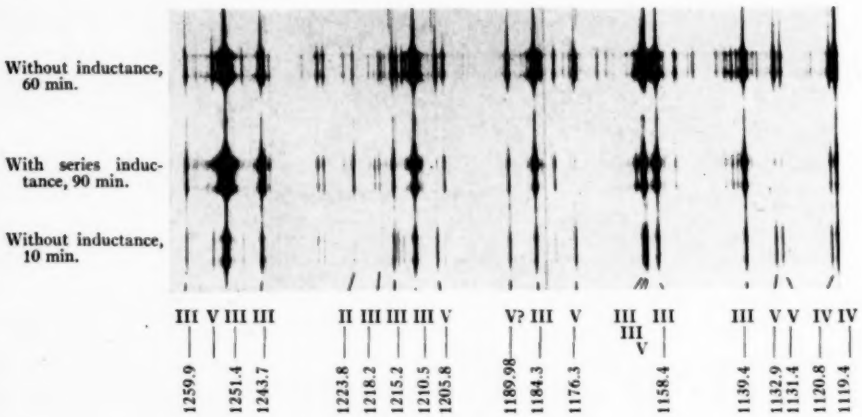

Fig. 3. Tin

than would be expected if only a Sn V line occupied that position. A line chosen by them at 1218.21A for Sn V belongs definitely to Sn III. Certain lines which Green and Loring[8] have picked for the spectrum of Sn III, but not completely identified belong to other states of ionization. Those at 1294.41A and at 1205.8A belong to Sn V.

We might go on citing other cases in these spectra in which the use of series inductance has made it reasonable to reject some lines in a given region and definitely to select certain others, as belonging to a particular multiplet. If one may then successfully apply the ordinary methods employed in classifying lines to the particular lines thus selected, he has more assurance that the identifications made in this way are correct. While the use of inductance in series with a vacuum spark furnishes useful evidence for classifying lines according to the stages of ionization of the atoms from which they come, it should not be concluded without further experimental verification that all lines arising from a given stage of ionization of an element are similarly modified by this change in the discharge circuit. Certain electronic transformations may be more sensitive to this change than others, or the lines of a given multiplet may show effects that are more marked than those of other multiplets. It is even conceivable, although not likely, that the lines of any one multiplet may thus be unequally affected. It is hoped that some of these questions may be answered by a more systematic study of the effect of series inductance upon many lines in various spectra, particularly upon those lines whose identification has been reliably determined by other criteria.

[7] Gibbs and White, Proc. Nat. Acad. Sci. **14**, 345 (1928).
[8] Green and Loring, Phys. Rev. **30**, 574 (1927).

THE EXCITATION OF THE ARC SPECTRUM OF NITROGEN

By O. S. Duffendack and R. A. Wolfe
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(Received April 24, 1929)

Abstract

The arc spectrum of nitrogen has been quite completely excited and measured in the region 8800–3400A with a low voltage arc in a mixture of helium and nitrogen. The process of excitation is probably a two step process: the first being the dissociation of nitrogen molecules into neutral atoms by impacts of the second kind with metastable helium atoms and the second, being the excitation of neutral nitrogen atoms by second impacts with metastable helium atoms. A complete list of wavelengths is given and the classifications of the lines designated as far as they are known. A considerable number of new lines have been classified.

Historical

DUE to the great stability of the nitrogen molecule the usual methods of excitation yield band spectra, attributed to the neutral or ionized nitrogen molecule, and a line spectrum attributed to ionized atoms. When dissociation is produced in electric discharges through nitrogen only a very small percentage of neutral atoms are formed, the greater portion being ionized. For this reason the usual methods of excitation have not yielded the arc spectrum because the light emitted by the neutral atoms must have been extremely feeble.

Several different methods have been used to obtain portions of the nitrogen arc spectrum. The results obtained have been to a certain extent uncertain. While working with a nitrogen filled canal ray tube Hardtke[1] noticed a few lines in the glow back of the cathode which he attributed to the neutral nitrogen atom. They were not separated from the spark lines, were very uncertain, and were measured only approximately. A little later Merril[2] and Kiess[3] published lines observed in the near infra-red which they obtained from nitrogen filled discharge tubes. The same lines were also obtained by them while observing the spectra of arcs and sparks in air between metallic electrodes.

The next work on the arc spectrum of nitrogen was done by Merton and Pilley[4] who used a Geissler tube discharge through a mixture containing an excess of helium and a trace of nitrogen. The first three lines which they observed in the far red corresponded to three lines observed by Merril[2] and by Kiess.[3] This fact alone led to a preliminary analysis of the spectrum by Kiess.[5]

[1] Hardtke, Ann. d. Physik **56**, 363 (1918).
[2] Merril, Astrophys. J. **51**, 236 (1920).
[3] Keiss, Publ. Amer. Astron. Soc. **4**, 170, 363 (1923).
[4] Merton and Pilley, Roy. Soc. Proc. **A107** 411 (1925)
[5] Keiss, J.O.S.A. **11**, 1 (1925).

At nearly the same time Fowler[6] published an analysis of the spark spectrum of nitrogen which contained none of these previously observed lines.

The method used by Merton and Pilley presented certain difficulties in the removal of foreign gases and the control of the nitrogen pressure because it was difficult to regulate the amount of nitrogen introduced. They had no means of measuring the amount and even a slight excess prevented the development of the arc lines. After the foreign gases were removed and the nitrogen was admitted the tubes were operated for some time during which the nitrogen gradually "cleaned up" in the discharge. Photographs were taken at intervals and some of them showed the nitrogen arc lines. Thus it was difficult to duplicate the conditions most favorable to the excitation of the spectrum. Long exposures were necessary and the disappearance of the gas made it impossible to obtain many exposures from a single tube.

Merton and Pilley[4] account for the emission of the nitrogen arc spectrum by assuming that the helium atoms act as "safety valves" which blow off when they are struck by electrons possessing 20.5 volts of energy. This would set an upper limit to the amount of energy that an electron would proabably attain. If we assume that the amount of energy necessary to excite the arc lines is less than 20.5 volts and to excite the spark lines more than this amount then it would appear that the above method would bring about the complete isolation of the nitrogen arc lines.

A second explanation, advanced by K. T. Compton,[7] is that the nitrogen molecules are dissociated into neutral atoms by impacts of the second kind with metastable helium atoms possessing 20.5 volts of energy. According to this view the helium atoms in the tube are raised to their 20.5 volt level by direct electron impacts. These metastable helium atoms may collide with neutral nitrogen molecules and dissociate them.

In order to observe the arc spectrum a considerable concentration of neutral nitrogen atoms is necessary. This would necessitate a large electron current through the gas in order to obtain a high concentration of excited helium atoms. In low voltage arcs in helium, a high concentration of helium atoms in a metastable state, has been demonstrated. This would result in a high concentration of neutral nitrogen atoms. The concentration of both would, therefore, be proportional to the electron current through the tube.

If a low partial pressure of nitrogen were not used the electrons would make inelastic collisions with the nitrogen molecules and cause the emission of the band spectra. With a high accelerating voltage the nitrogen molecules would be dissociated into ionized atoms by the inelastic collisions and cause the emission of the spark spectrum.

In view of the above suggestions it seems logical to expect that a low voltage arc should be a suitable means of exciting the arc spectrum of nitrogen. This method would enable one to obtain the high concentration of metastable helium atoms and at the same time sufficient ionization to permit large electron currents through the gas. Moreover there must exist uniquely

[6] Fowler, Roy. Soc. Proc. **A107**, 31 (1925).
[7] Compton, Phil. Mag. **50**, 512 (1925).

favorable pressures of the helium and the nitrogen to obtain the best results. The apparatus used with the low voltage arc give one a ready means of studying such conditions, since the partial pressures of both gases can be varied at will.

Experimental

A low voltage arc discharge tube of the conventional design was used in this investigation. The light emitted by the discharge was photographed through a quartz window. Three liquid air traps were connected close to the discharge tube, the center one containing charcoal. The evacuating system consisted of a double stage mercury pump backed by a Cenco Hyvac pump. The pressure inside the system was determined by a McLeod gauge. For purifying and reclaiming the helium a separate system was sealed on consisting of a charcoal trap, a Geissler tube containing magnesium, and a Toepler pump. Bulbs were provided for storing the purified helium and nitrogen.

After the entire system had been completely freed of foreign gases the helium was introduced. It was allowed to stand for an hour or more in contact with the charcoal, in the first trap, immersed in liquid air. At the same time a heavy discharge was passed through the Geissler tube containing magnesium. The gas was then pumped through a second charcoal trap, a second Geissler tube and "getter" and into a storage bulb. After the helium had passed three times through this purifying process it became very pure and at high pressures showed only a faint trace of hydrogen, the only impurity.

The nitrogen was generated outside the system. A chemically pure solution of sodium nitrite was added drop by drop to a similar solution of ammonium chloride while at the same time the latter solution was gently warmed. The gas so produced was passed through a concentrated solution of potassium hydroxide to absorb the carbon dioxide, then over phosphorus pentoxide to absorb the water vapor, and lastly through copper turnings, heated to 550°C, to remove the oxygen. The nitrogen so generated failed spectroscopically to show any trace of an impurity.

Before the purified gases were introduced into the system the tungsten filaments and discharge tube were freed of gases in the usual manner. Mercury vapor was removed with liquid air traps. The optimum pressures for the helium and the nitrogen were then determined.

It should be remembered in this connection that a high current density was expected to be most favorable to the production of atomic nitrogen. With this in view various helium pressures, ranging from a fraction of a millimeter to 30 millimeters, were tried. At low pressures not enough positive ions were formed to neutralize the space charge around the cathode and the current was space charge limited. At high pressures too high a voltage was required to produce the desired current. At a pressure of 11 millimeters, large currents, as high as 10 amperes at 90 to 100 volts, could be maintained through the tube, and this was selected as the most desirable helium pressure. With helium at this pressure in the discharge tube, nitrogen was

added in small amounts until the arc lines became most prominent. A slight excess of nitrogen brought out the negative bands strongly, covering up the arc lines. A higher percentage of dissociation was probably attained at extremely low nitrogen pressures but the feebleness of the emitted radiation made detection difficult. Best results seemed to be obtained when the negative bands were present with feeble intensity. The amount of nitrogen introduced varied in different spectral regions. In that portion of the visible region from 3400A to 6000A a partial pressure of about 0.01 millimeter was used. In the region around 8700A pressures as high as 0.1 millimeter were found to be most suitable.

As the discharge was run the nitrogen cleaned up quite rapidly on the filament, forming a brownish-black deposit, presumably of tungsten nitride. The nitrogen absorbed by the charcoal served as a reservoir and kept the partial pressure of the nitrogen in the mixture practically constant.

After the optimum pressures had been determined the usual method of procedure was as follows: Pure helium, at a pressure of about 11 millimeters, was introduced into the system. A potential difference of 90-100 volts was then then impressed upon the electrodes and the discharge started. Spectrograms were taken of the helium to determine its purity and to locate the helium band lines. The correct amount of nitrogen was then added and spectrograms taken under exactly similar conditions showing the nitrogen arc lines.

The Nitrogen Arc Spectrum

Theoretically a high current density is required for the formation of the nitrogen arc spectrum according to the explanation given by K. T. Compton[7] of this type of discharge. The first part of the work was done using a current of approximately 60 milliamperes through the tube. With such a small current the arc lines could not be detected even though a rapid spectrograph was employed and a high speed plate used. The current density could be increased readily enough by increasing the filament temperature, but such an increase in temperature quickly produced a "flare" condition. In order to limit the current through the tube a relay was placed in the plate circuit and set to operate at 250 milliamperes. This interruption of the arc prevented flare conditions and at the same time allowed the necessary current density. Although the relay interrupted the plate circuit when the meter indicated 250 milliamperes, the current through the tube was much in excess of this.

When the interrupted arc was used the region between the filament and plate showed the following characteristics: Spectrograms taken from a region direcly off of the filament showed well developed helium line and band spectra. Traces of nitrogen band edges were also present. Spectrograms taken from a region about 5 millimeters from the filament showed entirely different phenomena. At this point the helium lines were much weakened, the helium bands had in most cases completely disappeared, the nitrogen bands were slightly stronger, and a well developed arc spectrum of nitrogen appeared. This region was used in obtaining all the plates showing the arc lines. Spectrograms taken from a region just in front of the plate gave very few arc lines. The nitrogen bands and helium lines were very strong in this region

and helium bands were again present. The light photographed in this case came from a group of small tufts on the plate.

Determination of Wave-Lengths

The measurements were made from fine grained plates with a precision comparator. High magnification was used and the settings made as nearly as possible on the centers of the lines. Measurements were repeated on the same line to insure as great accuracy as possible. International iron lines were used for comparison.

Three different spectrographs were used during the investigation. For use in detecting faint radiations a two prism glass spectrograph and a Hilger E2 quartz spectrograph were used. The plates from which the lines were measured were taken with a Hilger E1 spectrograph. For work from 3200A to 5000A it was equipped with a quartz prism and lens. For work above 5000A it was equipped with a glass prism and lens. With the quartz prism the dispersion varied from 8A per millimeter at 3400A to 20A per millimeter at 5000A. Using the glass prism the dispersion varied from 4A per millimeter at 4000A to 25A per millimeter at 7000A.

In the lower part of the visible region the lines obtained by using the glass prism were sonewhat fuzzy and plates taken with the quartz system were measured. The upper glass region gave lines which were clear and sharp.

The length of exposures necessary varied with the region of the spectrum and the type of plate used. Using the quartz system, in the visible region, spectrograms could be obtained on fast plates in one hour. Strong lines were easily photographed in 10 minutes. With fine grained plates exposures of two hours were made in the same region. With the glass system and spectrum plates, exposures of 3 hours were needed in the region from 5000A-7000A. In the glass region from 7000A-8860A Eastman Neocyanine plates were used. Exposures of six hours were found necessary here.

Results

The measurements contained in the table were obtained as explained above. The lines listed from 3400A-5000A are believed to be correct to at least 0.03 of an angstrom unit with the exception of those lines which are marked with an intensity of 00 or with a ? mark. An accuracy of at least 0.05A is believed to exist from 5000A-6900A and 0.1A from 6900A out to the longest measured wave-length. All of the lines have been measured on at least two different plates and most of them on three plates. Average values are given but only those values were averaged that agreed within the above mentioned limits of accuracy. In case of doubt the line was remeasured. Shifts of spectral lines due to temperature changes were not noticed; due, no doubt, to the comparatively short exposures necessary. A few lines were confused with nitrogen band structure and are so marked. Diffuse lines are also indicated. The intensities listed are eye intensities. They are average intensities as judged from different plates, and different length exposures.

As will be noticed from the table several of the lines reported by Merton and Pilley[4] have not been observed. Changes in intensity have been noticed and as a rule are toward greater intensity. This increased intensity resulted,

no doubt, from the high current density which was maintained through the tube. Two or three lines reported by them as having considerable intensity could not be found, although a careful search was made on a large number of plates. The measured values in the table agree in most cases, within the limits of error, with Merton and Pilley's values. Hardtke[1] made no attempt to measure accurately the lines he observed. Several of the lines reported by Hardtke and not reported by Merton and Pilley have been found, but all such seem to have low intensity.

Due to the greater intensity of the source used spectrograms could be obtained on shorter exposures than with Geissler tubes. This prevented temperature shifts with the resulting broadening of the lines. Because of small dispersion the lines in the region around 8500A have been reported to only one decimal place. These lines were all found by Kiess. It is thought that more lines should be observed in the region around 6900A but plates sensitive in this region could not be found and the lines were not observed. Lines due to helium bands and nitrogen bands have been eliminated and no spark lines were obtained.

Conclusion

The writers believe that the present method shows marked superiority over the previous methods used in the excitation of the arc spectrum of nitrogen. The relative ease with which the helium can be purified and the ability to control the gas pressures seem to be distinct advantages. Since the work was done with a comparatively low pressure of helium fewer helium bands were formed, as they are generally recognized as high pressure bands. While photographing the arc spectrum they usually completely disappeared.

It should be mentioned at this point that Duffendack[8] and Duncan[9] failed to excite the nitrogen arc lines by using direct electron impacts with 20.5 volt electrons. This would seem to exclude the possibility that 20.5 volts of energy constitutes the best excitation voltage for the arc lines. It is probable, however, that the above writers might have observed arc lines in the region of longer wave-lengths.

When the nitrogen arc lines were obtained most readily the tungsten filament decomposed rapidly forming a brownish-black deposit on the leads. As normal nitrogen does not react with tungsten, the abnormal wasting of the filament suggests that active nitrogen was present. Under these conditions even strong spark lines were missing so its seems reasonable to suppose that the active nitrogen was due to neutral atomic nitrogen and not to ionized nitrogen atoms. Moreover, low voltage arcs in pure nitrogen do not show an abnormal wasting away of the filament. When an excess of nitrogen was mixed with the helium, and the mixture excited, the tungsten leads functioned normally. Thus the active nitrogen must have been due to neutral atoms.

Merton and Pilley reported 114 lines. Of these 28 were reported by Hardtke. Hardtke reported 15 lines not found by Merton and Pilley. We have found 230 lines. All but 7 of the lines reported by Merton and Pilley

[8] Duffendack, Phys. Rev. **20**, 665 (1922).
[9] Duncan, Astrophys. J. **62**, 145 (1925).

have been found and 13 additional lines reported by Hardtke and not found by Merton and Pilley. Two of Hardtke's lines remain unverified. Kiess reported 21 lines, three of which were observed by Merton and Pilley. All of these lines have been observed. This leaves in addition 90 lines not previously reported. Since these results were reported at the Chicago meeting of the American Physical Society[10] Ryde has reported a considerable number of the same lines.[11]

The excitation of the arc lines of nitrogen in our discharge, and likewise in Merton and Pilley's, is probably a two step process. The first step is undoubtedly the dissociation of a nitrogen molecule into two neutral atoms. The dissociation of a molecule into a normal atom and an atom excited to one of the initial levels involved in the lines here reported is impossible by this process because an excited helium atom does not possess sufficient energy to do this. The lowest value of the heat of dissociation of a normal nitrogen molecule for which there is any basis[12] is 9.1 volts and the lowest initial level of the lines reported is that of the $3p^1D_1$ which has an excitation potential of 11.7 volts. Hence 20.8 volts energy is required to dissociate a nitrogen molecule and excite the lines originating in the *lowest* term while a metastable helium atom possesses not more than 20.5 volts energy.

The question then arises as to what is the second step in the excitation process. Two possibilities at once suggest themselves; an electron impact, and a second impact of the second kind. The electron current density in the region of the discharge under consideration was fairly large and the electrons possessed in general, sufficient energy to excite the lines. But the concentration of nitrogen atoms must have been very small; because, in the first place the partial pressure of the nitrogen was usually about 0.01 mm and never more than 0.1 mm and in the second place not all of the nitrogen in this region was atomic. The excitation of the negative bands of nitrogen, belonging to the nigrogen molecule ion, revealed the presence of molecular nitrogen and their intensity leads us to believe that probably not over half the nitrogen in this region was dissociated. As only 0.1 percent to 1 percent of the gas mixture was nitrogen, only one electron impact in a thousand or at most one in a hundred could have involved a nitrogen atom or molecule. Therefore, if the lines were excited by electron impacts, their intensities would be expected to be very low compared with the intensities of the helium lines. While in general the nitrogen lines were weaker than the helium lines, the difference in their intensities was not great.

Another reason for believing that the nitrogen lines were not excited by electron impacts is that the neutral or positive bands of nitrogen were lacking. Since molecular nitrogen must have been present in a concentration at least comparable with that of atomic nitrogen, as revealed by the negative bands in the spectrum, one must account for the failure of the positive bands to appear. The excitation potentials of the positive bands[9] are of the same order as of the arc lines and hence should have been excited by the same stream of electrons. But the positive bands were absent while the negative

[10] Duffendack and Wolfe, Phys. Rev. **29**, 209 (1927).
[11] Ryde, Roy. Soc. Proc. **A117**, 164 (1927).
[12] Kaplan, Phys. Rev. **33**, 638 (1929).

bands of higher excitation potentials appeared. The presence of the negative bands and absence of the positive bands leads us to suspect that nitrogen molecules were simultaneously ionized and excited by impacts with metastable helium atoms or helium ions. A similar excitation of the negative bands of carbon monoxide has been observed by Duffendack and Smith[13] in a mixture with helium. Their investigation shows that excitation of negative bands by this process is very great compared with that of the positive and negative bands by electron impacts when helium is the preponderant element of the gas mixture. The reason that the positive nitrogen bands are not excited by metastable helium atoms is that their excitation potentials are considerably below those of the helium atom, whereas the difference between the excitation potentials of the negative bands and the helium atom is less than one volt. Hence the probability that the negative bands would be excited instead of the positive bands is very great. The conclusion from this reasoning is that the nitrogen arc lines were probably not excited by electron impacts and hence must have resulted from second impacts of the second kind with metastable helium atoms.

The view that the nitrogen arc lines were excited by impacts of the second kind with metastable helium atoms aids in an accounting for some of the unclassified lines of the accompanying list. A study of the table shows that there are two important groups yet to be classified, one in the region of 4700A and the other in the region below 4350A. The former group comes at the place where lines for the transition $4p^2(P, D)$ to $3s^2\,P$ would be expected from a consideration of the terms now known with certainty. There is, however, no place for the group in the region below 4350A in the spectrum built on the terms listed in the accompanying paper by Dr. Ingram. But it can be predicted from the Hund theory that there are other terms in the N I spectrum. A series of doublet terms converging at the metastable ^1D term of N II should be fairly important and all of these except the first ones will have negative values and hence high excitation potentials. It would seem quite probable that the unclassified lines in the region below 4350A may belong to the doublet terms of this series. Metastable helium atoms have sufficient energy for their excitation.

Some explanation is needed with regard to the following table. The wavelengths given in the first column are our measurements except for those marked #. Lines marked thus were not found on our plates or were obscured by nearby helium lines or band structure. The intensities given are estimated relative eye intensities as determined from several plates. The letters in the third column indicate other observers who found the same line. The classifications in the last column are those previously published except those marked* which are new. The new classifications are due mainly to Dr. Ingram and the reasons for the assignments are discussed in his paper, which follows. The table has been made as complete as possible for the convenience of those interested in this spectrum.

We wish to acknowledge our indebtedness to the U. S. Bureau of Mines for helium used in this investigation.

[13] Duffendack and Smith, Phys. Rev. **34**, 68 (1929).

TABLE I.

Wave-lengths. (I.A.)	Intensity.	Wave-numbers (vacuum)	Other observers	Classification
8729.1	1	11452.79	C	$3s^4P_{1\frac{1}{2}} - 3p^4D_{\frac{1}{2}}$
8719.0	2	11466.06	C	$3s^4P_{2\frac{1}{2}} - 3p^4D_{2\frac{1}{2}}$
8711.9	2	11475.42	C	$3s^4P_{1\frac{1}{2}} - 3p^4D_{1\frac{1}{2}}$
8703.4	2	11486.60	C	$3s^4P_{\frac{1}{2}} - 3p^4D_{\frac{1}{2}}$
8686.4	3	11509.11	C	$3s^4P_{\frac{1}{2}} - 3p^4D_{1\frac{1}{2}}$
8683.6	4	11512.79	C	$3s^4P_{1\frac{1}{2}} - 3p^4D_{2\frac{1}{2}}$
8680.3	5	11517.18	C	$3s^4P_{2\frac{1}{2}} - 3p^4D_{3\frac{1}{2}}$
8656.3	2	11549.18	C	$3s^2P_{1\frac{1}{2}} - 3p^2P_{\frac{1}{2}}$
8629.5	4	11585.00	C	$3s^2P_{1\frac{1}{2}} - 3p^2P_{1\frac{1}{2}}$
8594.3	3	11632.42	C	$3s^2P_{\frac{1}{2}} - 3p^2P_{\frac{1}{2}}$
8568.1	2	11668.00	C	$3s^2P_{\frac{1}{2}} - 3p^2P_{1\frac{1}{2}}$
8242.5	4	12128.94	C	$3s^4P_{2\frac{1}{2}} - 3p^4P_{1\frac{1}{2}}$
8223.3	5	12157.28	C	$3s^4P_{1\frac{1}{2}} - 3p^4P_{\frac{1}{2}}$
8216.45	7	12167.36	C	$3s^4P_{2\frac{1}{2}} - 3p^4P_{2\frac{1}{2}}$
8210.9	3	12175.59	C	$3s^4P_{1\frac{1}{2}} - 3p^4P_{1\frac{1}{2}}$
8200.6	1	12190.89	C	$3s^4P_{\frac{1}{2}} - 3p^4P_{\frac{1}{2}}$
8188.2	5	12209.24	C	$3s^4P_{\frac{1}{2}} - 3p^4P_{1\frac{1}{2}}$
8185.0	5	12214.11	C	$3s^4P_{1\frac{1}{2}} - 3p^4P_{2\frac{1}{2}}$
7468.7	9	13385.54	C B	$3s^4P_{2\frac{1}{2}} - 3p^4S_{1\frac{1}{2}}$
7442.6	9	13432.47	C B	$3s^4P_{1\frac{1}{2}} - 3p^4S_{1\frac{1}{2}}$
7423.9	5	13466.32	C B	$3s^4P_{\frac{1}{2}} - 3p^4S_{1\frac{1}{2}}$
6982.02	00	14318.56		$3p^4P_{1\frac{1}{2}} - 5s^4P_{\frac{1}{2}}$*
6979.10	1	14324.55		$3p^4P_{2\frac{1}{2}} - 5s^4P_{1\frac{1}{2}}$*
6951.50	1	14381.42		$3p^4P_{\frac{1}{2}} - 5s^4P_{1\frac{1}{2}}$*
6945.22	4	14394.43	B	$3p^4P_{2\frac{1}{2}} - 5s^4P_{2\frac{1}{2}}$
6926.90	1	14432.50	b	$3p^4P_{1\frac{1}{2}} - 5s^4P_{2\frac{1}{2}}$
6874.30	1	14543.93	B	
6793.82	00d	14715.21		$3p^4P_{2\frac{1}{2}} - 4d^4F_{3\frac{1}{2}}$*
6777.36	00d	14750.94		
6769.57	00d	14767.92		
6758.60	4	14791.89		$3p^4P_{1\frac{1}{2}} - 4d^4D_{2\frac{1}{2}}$*
6752.40	4	14805.47		$3p^4P_{2\frac{1}{2}} - 4d^4D_{3\frac{1}{2}}$*
6741.29	3	14829.87		$3p^4P_{1\frac{1}{2}} - 4d^4P_{\frac{1}{2}}$*
6733.48	6	14847.07	B	$3p^4P_{\frac{1}{2}} - 4d^4P_{\frac{1}{2}}$*
6723.12	9	14869.95	B	$3p^4P_{2\frac{1}{2}} - 4d^4P_{2\frac{1}{2}}$*
6713.12	1	14892.10	B	
6708.81	4	14901.67	B	
6706.20	4	14907.47	B	$3p^4P_{1\frac{1}{2}} - 4d^4P_{2\frac{1}{2}}$*
6666.75	0d	14995.68		$3p^2P_{1\frac{1}{2}} - 5d^2P_{1\frac{1}{2}}$*
6656.61	1	15018.52	B	$3p^4D_{1\frac{1}{2}} - 5s^4P_{\frac{1}{2}}$
6653.41	5	15025.75	B	$3p^4D_{2\frac{1}{2}} - 5s^4P_{1\frac{1}{2}}$
6646.52	2	15041.32	B	$3p^4D_{\frac{1}{2}} - 5s^4P_{\frac{1}{2}}$
6644.96	9	15044.85	B	$3p^4D_{2\frac{1}{2}} - 5s^4P_{2\frac{1}{2}}$
6637.01	4	15062.87	B	$3p^4D_{1\frac{1}{2}} - 5s^4P_{1\frac{1}{2}}$
6627.02	0	15085.58	B	$3p^4D_{\frac{1}{2}} - 5s^4P_{1\frac{1}{2}}$
6622.53	3	15095.81	B	$3p^4D_{2\frac{1}{2}} - 5s^4P_{2\frac{1}{2}}$
6612.63	00?	15118.41		
6606.77	00	15131.82		$3p^4D_{1\frac{1}{2}} - 5s^4P_{2\frac{1}{2}}$?*
6580.70	0	15191.76		
6544.77	0d	15275.16		
6534.12	0d	15300.05		
6506.45	0	15365.13		$3p^4D_{3\frac{1}{2}} - 4d^4F_{4\frac{1}{2}}$*
6499.52	3	15381.51	B	$3p^4D_{3\frac{1}{2}} - 4d^4F_{3\frac{1}{2}}$
6491.28	3	15401.03	B	$3p^4D_{2\frac{1}{2}} - 4d^4F_{2\frac{1}{2}}$
6484.88	9	15416.23	B	$3p^4D_{3\frac{1}{2}} - 4d^4F_{3\frac{1}{2}}$
6483.75	3	15418.92	B	$3p^4D_{1\frac{1}{2}} - 4d^4F_{2\frac{1}{2}}$
6482.74	9	15421.32	B	$3p^4D_{3\frac{1}{2}} - 4d^4F_{4\frac{1}{2}}$
6481.73	2	15423.73	B	$3p^4D_{\frac{1}{2}} - 4d^4F_{1\frac{1}{2}}$
6480.50	0	15426.65	B	$3p^4D_{1\frac{1}{2}} - 4d^4D_{\frac{1}{2}}$
6471.03	1	15449.23	B	$3p^4D_{\frac{1}{2}} - 4d^4D_{\frac{1}{2}}$
6468.32	4	15455.70	B	$3p^4D_{3\frac{1}{2}} - 4d^4D_{3\frac{1}{2}}$ $3p^4D_{2\frac{1}{2}} - 4d^4D_{2\frac{1}{2}}$
6462.83	0	15468.83	B	

TABLE I. (Continued)

Wave-lengths (I.A.)	Intensity	Wave-numbers (vacuum)	Other observers	Classification
6457.93	3	15480.57	B	$3p^4D_{1\frac{1}{2}}-4d^4D_{1\frac{1}{2}}$
6452.75	1	15493.00	B	$3p^4D_{1\frac{1}{2}}-4d^4D_{2\frac{1}{2}}$
6448.49	0	15503.23	B	$3p^4D_{\frac{1}{2}}-4d^4D_{1\frac{1}{2}}$
6441.70	5	15519.57	B	$3p^4D_{2\frac{1}{2}}-4d^4P_{2\frac{1}{2}}$
6440.95	3	15521.38	B	
6437.01	4	15530.88	B	$3p^4D_{1\frac{1}{2}}-4d^4P_{\frac{1}{2}}$*
6428.05	00	15552.53		$3p^4D_{\frac{1}{2}}-4d^4P_{\frac{1}{2}}$*
6422.93	3	15564.93		
6420.47	3	15570.89	B	$3p^4D_{2\frac{1}{2}}-4d^4P_{2\frac{1}{2}}$
6417.05	2	15579.19	B	
6411.53	0	15592.60		
6321.70	00	15814.17		$3p^4S_{1\frac{1}{2}}-6s^4P_{\frac{1}{2}}$*
6303.68	0	15859.37	B	$3p_4S_{1\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$
6298.30	0	15872.92		
6289.27	00	15895.71		
6285.78	1	15904.53	B	
6283.06	00	15911.42		
6279.42#	—	15920.63	B	
6275.43	1	15930.77	B	$3p^4S_{1\frac{1}{2}}-6s^4P_{2\frac{1}{2}}$
6272.83	1	15937.37	B	$3p^2D_{2\frac{1}{2}}-5d^2P_{1\frac{1}{2}}$*
6075.83	3	16454.11	B	
6017.70	2	16613.05	B	
6015.40	1	16619.41		
6008.48	10	16638.54	B	$3p^2S_{\frac{1}{2}}-4d^2P_{1\frac{1}{2}}$*
5999.47	6	16663.53	B	$3p^2S_{\frac{1}{2}}-4d^2P_{\frac{1}{2}}$*
5962.15	00	16767.84		
5941.94	0	16824.87		
5927.50	0	16865.86		
5856.23	1	17071.11		$3p^4P_{1\frac{1}{2}}-6s^4P_{\frac{1}{2}}$*
5854.16	2	17077.15		$3p^4P_{2\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$*
5841.01	2	17115.59		$3p^4P_{1\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$*
5834.71	1	17134.07	A	$3p^4P_{\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$*
5829.53	6	17149.30	B	$3p^4P_{2\frac{1}{2}}-6s^4P_{2\frac{1}{2}}$
5816.48	2	17187.78		$3p^4P_{1\frac{1}{2}}-6s^4P_{2\frac{1}{2}}$*
5793.51	1	17255.92		
5752.64	4	17378.52	B	$3p^4P_{2\frac{1}{2}}-5d^4P_{2\frac{1}{2}}$*
5747.36	2	17394.48		$3p^4S_{1\frac{1}{2}}-7s^4P_{2\frac{1}{2}}$*
5740.65	2	17414.81		
5735.63	1	17430.05		
5710.77#	–	17505.93	B	
5694.24	0	17556.75		
5686.19	0	17581.60	B	
5667.04	1	17641.01		
5648.68	0	17698.35		
5625.43	2	17771.50	B	$3p^4D_{1\frac{1}{2}}-6s^4P_{\frac{1}{2}}$
5623.20	4	17778.55	B	$3p^4D_{2\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$
5618.18	1	17794.44	B	$3p^4D_{\frac{1}{2}}-6s^4P_{\frac{1}{2}}$
5616.54	5	17799.63	B	$3p^4D_{2\frac{1}{2}}-6s^4P_{2\frac{1}{2}}$
5611.36	1	17816.06	B	$3p^4D_{1\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$
5604.28	0	17838.57		$3p^4D_{\frac{1}{2}}-6s^4P_{1\frac{1}{2}}$*
5600.54	0	17850.48		$3p^4D_{2\frac{1}{2}}-6s^4P_{2\frac{1}{2}}$*
5567.63#	1	17955.97	B	
5564.37	9	17966.51	A B	$3p^4D_{2\frac{1}{2}}-5d^4F_{3\frac{1}{2}}$?*
5563.84#	3d	17968.21	B	
5560.37	9	17979.44	A B	$3p^4D_{3\frac{1}{2}}-5d^4F_{4\frac{1}{2}}$?*
5557.44	2	17988.92	B	
5551.34	0d	18008.68		
5548.18	00	18018.93		
5545.11	3	18028.91	A B	$3p^4D_{3\frac{1}{2}}-5d^4P_{2\frac{1}{2}}$*
5540.36	1	18044.37		
5535.37	1	18060.64		
5530.10	0d	18077.85		

TABLE I. (Continued)

Wave-lengths (I.A.)	Intensity	Wave-numbers (vacuum)	Other observers	Classification
5378.45	0	18587.56	B	$sp^4\,^4P_{\frac{1}{2}} - 4p^4D_{\frac{1}{2}}{}^*$
5372.66	3d	18607.59	A B	$sp^4\,^4P_{\frac{3}{2}} - 4p\,^4D_{1\frac{1}{2}}{}^*$
5371.10	1	18613.00		$3p^4P_{2\frac{1}{2}} - 7s^4P_{2\frac{1}{2}}{}^*$
5367.27	1	18626.28	A B	$sp^4\,^4P_{1\frac{1}{2}} - 4p^4D_{1\frac{1}{2}}{}^*$
5356.77	5	18662.78	A B	$sp^4\,^4P_{1\frac{1}{2}} - 4p^4D_{2\frac{1}{2}}{}^*$
5344.23	00	18706.58		$sp^4\,^4P_{2\frac{1}{2}} - 4p^4D_{2\frac{1}{2}}{}^*$
5334.42	1	18740.98		$3p^4P_{2\frac{1}{2}} - 6d^4P_{2\frac{1}{2}}{}^*$
5328.70	5	18761.10	A B	$sp^4\,^4P_{2\frac{1}{2}} - 4p^4D_{3\frac{1}{2}}{}^*$
5310.52	1	18825.32	B	$sp^4\,^4P_{\frac{1}{2}} - 4p^4P_{1\frac{1}{2}}{}^*$
5309.48	1	18829.01	A B	$sp^4\,^4P_{1\frac{1}{2}} - 4p^4P_{\frac{1}{2}}{}^*$
5292.75	0d	18888.53	A B	$\begin{cases} sp^4\,^4P_{2\frac{1}{2}} - 4p^4P_{1\frac{1}{2}}{}^* \\ sp^4\,^4P_{1\frac{1}{2}} - 4p^4P_{2\frac{1}{2}}{}^* \end{cases}$
5281.18	3	18929.91	A B	$sp^4\,^4P_{2\frac{1}{2}} - 4p^4P_{2\frac{1}{2}}{}^*$
5201.71	2	19219.11	B	$3p^2S_{\frac{1}{2}} - 5d^2P_{1\frac{1}{2}}{}^*$
5200.00	0	19225.43		
5197.00#	00	19236.53	B	
5189.51	1	19264.29		$3p^4D_{3\frac{1}{2}} - 7s^4P_{2\frac{1}{2}}?{}^*$
5181.47	0	19294.18	A	$sp^4\,^4P_{1\frac{1}{2}} - 4p\,^4S_{1\frac{1}{2}}{}^*$
5179.61	00	19301.11		
5169.45	1	19339.05	A	$sp^4\,^4P_{2\frac{1}{2}} - 4p^4S_{1\frac{1}{2}}{}^*$
5162.78	1	19364.03		
4935.03	10	20257.68	A B	$3s^2P_{1\frac{1}{2}} - 4p^2S_{\frac{1}{2}}$
4914.90	5	20340.63	A B	$3s^2P_{\frac{1}{2}} - 4p^2S_{\frac{1}{2}}$
4886.30	2	20459.69		
4881.79	1	20478.58	B	
4868.92	00	20532.72	B	
4855.43#	0d	20589.77	B	
4847.38	2	20623.96		
4837.93	1	20664.24		
4831.16	1d	20693.20	B	
4753.13	2	21032.91	B	
4750.26	2	21045.62	B	
4744.04	3?	21073.20		
4742.90	2	21078.27	B	
4736.04	0	21108.80	B	
4734.20	0	21117.00		
4731.22	1	21130.30		
4685.74	3	21335.39		
4669.77	3	21408.36	A	
4660.05	2	21453.01	A	
4657.72	1	21463.74		
4656.65	1	21468.68		
4651.08	1	21494.39		
4625.61	1	21612.74		
4554.21	1	21951.57		
4553.38	1	21955.58		
4503.53	1	22198.60		
4502.27	2	22204.82		
4499.08	0	22220.56		
4497.45	1	22228.60		
4494.67	5	22242.35	B	
4492.40	7	22253.59	B	
4485.09	0	22289.86	A	
4466.56	0	22382.34	A	
4365.80	0	22898.90		
4358.27	10	22938.46	B	
4343.41	1	23016.94		
4336.48	5	23053.71	A B	
4324.89	0	23115.49	A	
4321.99	1	23131.01		
4317.70	5	23153.99	A B	
4313.11	4	23178.63	A B	
4305.46	6	23219.82	A B	

TABLE I. (Continued)

Wave-lengths (I.A.)	Intensity	Wave-numbers (vacuum)	Other observers	Classification
4284.92	2	23331.12	B	
4282.20#	1	23345.92	B	
4281.39	2	23350.35	B	
4253.28	4	23504.68	B	$3s^4P_{2\frac{1}{2}}-4p^4D_{3\frac{1}{2}}^*$
4236.04	0	23600.33		
4230.35	4	23632.07	B	$3s^4P_{2\frac{1}{2}}-4p^4P_{1\frac{1}{2}}^*$
4229.59	2	23636.32		
4224.74	4	23663.45	B	$3s^4P_{1\frac{1}{2}}-4p^4P_{\frac{1}{2}}^*$
4223.04	5	23672.98	A B	$3s^4P_{2\frac{1}{2}}-4p^4P_{2\frac{1}{2}}^*$
4220.79	2	23685.60		
4215.92	2	23712.96	A	$3s^4P_{\frac{1}{2}}-4p^4P_{1\frac{1}{2}}^*$
4214.73	5	23719.65		$3s^4P_{1\frac{1}{2}}-4p^4P_{2\frac{1}{2}}^*$
4213.0#	–	23729.4	A	
4209.05	1	23751.67		
4206.29	1	23767.26		
4205.65	2d	23770.86		
4193.49	3	23839.79	A	
4187.06	1d	23876.40	A	
4180.0#	–	23916.7	A	
4166.64	1	23993.41	A	
4164.74	0	24004.36		
4151.46	12	24081.15	A B	$3s^4P_{2\frac{1}{2}}-4p^4S_{1\frac{1}{2}}^*$
4145.78	2	24114.14	A	
		[24127.87]	obscured by helium	$3s^4P_{1\frac{1}{2}}-4p^4S_{1\frac{1}{2}}^*$
4137.63	7	24161.64	A B	$3s^4P_{\frac{1}{2}}-4p^4S_{1\frac{1}{2}}^*$
4129.16	1	24211.20		
4114.00	6	24300.41	A B	$3s^2P_{1\frac{1}{2}}-(^1D)3p\,^2D_{1\frac{1}{2}}$
4109.98	12	24324.18	A B	$3s^2P_{1\frac{1}{2}}-(^1D)3p\,^2D_{2\frac{1}{2}}$
4102.18	2	24370.43		
4099.94	9	24383.74	A B	$3s^2P_{\frac{1}{2}}-(^1D)3p\,^2D_{1\frac{1}{2}}$
4041.30	0	24737.55		
4037.35	1	24761.75	B	
4033.64	1	24784.53		
4019.10	0	24874.19		
4015.08	0	24899.09		
4010.99	2	24924.48	A B	
4001.65	1	24982.66		
3999.98	4	24993.08	B	
3994.86	3	25025.11		
3969.95	1	25182.14		
3957.20	3	25263.27	B	
3952.21	3	25295.17	B	
3869.10	4	25838.51	B	
3834.84	2	26069.34		
3834.24	4	26073.42	B	$3s^2P_{1\frac{1}{2}}-(^1D)3p^2P_{\frac{1}{2}}$
3830.39	9	26099.63	B	$3s^2P_{1\frac{1}{2}}-(^1D)3p^2P_{1\frac{1}{2}}$
3822.07	6	26156.44	B	$3s^2P_{\frac{1}{2}}-(^1D)3p^2P_{\frac{1}{2}}$
3818.27	2	26182.47	B	$3s^2P_{\frac{1}{2}}-(^1D)3p^2P_{1\frac{1}{2}}$
3687.88	2	27108.16		
3681.10	3	27158.09	B	
3650.19	5	27388.06	B	
3545.62	2	28195.79	B	
3532.65	4	28299.30	B	
3437.14	4	29085.64	B	
Classified lines measured by Ryde.				
5304.9	1	18845.3		$sp^4\,^4P_{1\frac{1}{2}}-4p^4P_{1\frac{1}{2}}^*$
5187.1	1	19273.2		$sp^4\,^4P_{\frac{1}{2}}-4p^4S_{1\frac{1}{2}}^*$
4254.7	4	23496.5		$3s^4P_{1\frac{1}{2}}-4p^4D_{2\frac{1}{2}}^*$ and $3s^4P_{\frac{1}{2}}-4p^4D_{1\frac{1}{2}}^*$
4143.4	–	24127.87		$3s^4P_{1\frac{1}{2}}-4p^4S_{1\frac{1}{2}}^*$

A—Hardtke
B—Merton and Pilley
C—Kiess

CLASSIFICATION OF THE ARC SPECTRA OF NITROGEN AND CARBON

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Abstract

Infra-red work.—A carbon arc in air run at 125 amperes served to produce the arc spectra of carbon and nitrogen with great intensity. Using an infra-red spectrometer with a plane grating and a vacuum thermopile the wave-lengths and approximate intensities of about one hundred and twenty-five lines between 9000A and 20000A have been measured. About ninety of these lines are classified as combinations between terms in carbon I and in nitrogen I. A number of new terms are fixed in both of these spectra and many of the terms provisionally identified by Fowler and Selwyn in C I and by Compton and Boyce in N I are definitely confirmed.

Classification in the visible spectrum of nitrogen I.—Using data obtained by Duffendack and Wolfe a number of lines have been classified in the visible spectrum of nitrogen I. Reasons are given for changing the previous designations of the ^2P and ^2D terms found by Kiess at 5100 and 6800 respectively. These are assigned to the $2s^22p^2 \cdot 3p$ configuration and are considered as being based on the ^1D term of nitrogen II. A complete term table of nitrogen I is given.

THE arc spectrum of nitrogen was partially analyzed by Kiess[1] who found a number of multiplets in the visible and photographic infra-red regions. His work was extended by Hopfield[2] who found the combination of Kiess's terms with the ground term in the extreme ultra-violet, by Bowen,[3] and more recently by Compton and Boyce[4] who have given a fairly complete analysis of the extreme ultra-violet spectrum, including many high members of series in both the doublet and quartet systems.

The arc spectrum of carbon has been analyzed by Bowen[3] in the extreme ultra-violet region and by Fowler and Selwyn[5] in the extreme ultra-violet, visible and photographic infra-red regions. In a recent note Jog[6] reports three intercombination lines.

The measurement and analysis of these spectra in the infra-red region are important for several reasons. The greater number of the strong lines arising from transitions between the high terms lie between 10000A and 15000A where they cannot be observed photographically. There are many terms which do not combine to give lines in the extreme ultra-violet and which can only be found by studying the infra-red region. Finally, owing to the simplic-

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[1] Kiess, J.O.S.A. and R.S.I. **11**, 1 (1925).
[2] Hopfield, Phys. Rev. **27**, 801 (1926).
[3] Bowen, Phys. Rev. **29**, 231 (1927).
[4] Compton and Boyce, Phys. Rev. **33**, 145 (1929).
[5] Fowler and Selwyn, Roy. Soc. Proc. **A118**, 34 (1928).
[6] Jog, Nature **123**, 318 (1929).

ity of the extreme ultra-violet spectrum many of the terms which have been found have been determined on the basis of one combination only and hence must be considered as only tentative until they have been checked by cross combinations. These cross combinations in nearly all cases lie in the infra-red.

Experimental

Ryde[7] has shown that a carbon arc in air, when run at sufficiently high current densities, brings out strongly the arc spectra of carbon, nitrogen and oxygen. Such a source has decided advantages for infra-red work because of its great intensity. In the present work currents of about 125 amperes were used. In agreement with Ryde's observation it has been found that it was not feasible to use solid carbon poles because the arc at high currents becomes very unsteady and blows itself out. By substituting a cored carbon at the negative pole a great increase in steadiness was obtained. The carbons used were manufactured by the National Carbon Company for industrial purposes. I am indebted to Mr. A. C. Downes of the research laboratories of that company for a complete list of the impurities to be expected in such carbons. It is not certain that all the lines measured and not classified are due to carbon and nitrogen but potassium is the only one of the impurities

Fig. 1. Diagram of infra-red apparatus.

which has been definitely observed and it is probable that the lines of the others are too weak to be detected.

Figure 1 gives, diagrammatically, the optical system of the infra-red spectrometer. An image of the source is focussed on the slit S_1. The beam is collimated by the concave mirror M_1 and falls as a parallel beam on the plane grating G. It is diffracted and comes back again to M_1 which focusses it on the slit S_2. An image of this slit is formed by the concave mirror M_3 on the junctions of the thermopile T. The mirror M_1 has a focal length of one-half meter and the grating used in this work had 14400 lines per inch. The grating is placed on a spectrometer table so that its orientation may be readily measured. The wave-lengths are determined from the simple equation[8] $\lambda = k \sin\theta$ where θ is the difference between the readings on the spectrometer circle when the central image and the line in question respectively are focussed on the slit S_2. The constant k is determined by setting on a known line e. g. Hg 10139.75A.

For detecting the radiation a linear vacuum thermopile designed and built in this laboratory by Professor Firestone was used. The currents from this device were amplified about one hundred times by means of a Moll

[7] Ryde, Roy. Soc. Proc. **A117**, 164 (1927).

[8] Sleator, Astrophys. J. **48**, 125 (1918) derives this equation.

thermo-relay built by Kipp and Sons, Delft, and then read on an ordinary moving coil galvanometer.

With the grating used the region between 7000A and 30000A could be studied. Many of the lines could be measured in the second order and a few in the third. The presence of ghosts in the higher orders so complicated the spectrum beyond 20000A that the advantages which might be obtained by working in high orders under certain conditions were here somewhat reduced. Practically all of the strong lines in the spectrum studied, however, fell below 20000A so that the measurements in the first order were not impaired. About one hundred and twenty-five lines were measured altogether. The complete list is given in Table III. The intensities are given in mm of deflection on the galvanometer scale. Because of the unsteadiness of the arc they are only approximate, say to within a factor 2. The lines of nitrogen and carbon previously measured by others in the photographic infra-red have been measured here in the first and second orders. A comparison indicates that the absolute values of the wave-lengths are ordinarily accurate to 2A. Owing to the great intensity of the heavy current arc source it has been possible to use slit widths as small as 0.2 mm. This corresponds to about 5A in the region near 10000A. Using such slit widths lines as close as 7A have been clearly resolved in the first order.

To reduce the wave-lengths to vacuum the table given by Fowler in his "Report on Series in Line Spectra" has been used.

Spectrum of Nitrogen I

The preceding paper by Duffendack and Wolfe describes a method for developing the arc spectrum of nitrogen in a mixture with helium. Using the list of wave-lengths determined by these authors and published in their paper it has been possible to make a number of identifications in the visible spectrum of nitrogen I. In the table of wave-lengths included in that paper the designations of these lines are indicated in the last column. Both Kiess's identifications and those made in the present work are given. The new ones are denoted by an asterisk. A few of Ryde's unidentified lines fall at the positions predicted by the analysis and these have been included in the wave-length list.

Table I is a complete term table of the nitrogen arc spectrum as far as it is now known. The terms are grouped according to electronic configurations Most of the terms are based on the ^3P state of N II. A few which are based on ^1D have been so designated. Those which are new are indicated by an asterisk. A number of other terms determined by Compton and Boyce from extreme ultra-violet measurements have been slightly altered to bring them into somewhat better agreement with the more accurate infra-red data. These are distinguished by two asterisks. The rest of the terms have been taken directly from the work of Kiess, Bowen and Compton and Boyce. Since no intercombinations are known the doublet and quartet values are not expressed accurately relative to each other.

TABLE I. *Term values in nitrogen I.*

		$2s^22p^3$	
$2p^4S_{1\frac{1}{2}}$	117345	$2p^3D_{3\frac{1}{2},1\frac{1}{2}}$	98143
		$2p^3P_{1\frac{1}{2},\frac{1}{2}}$	88537
		$2s\,2p^4$	
$sp^4\,^4P_{2\frac{1}{2}}$	29235.5**		
$sp^4\,^4P_{1\frac{1}{2}}$	29191.6**		
$sp^4\,^4P_{\frac{1}{2}}$	29172.0**		
		$2s^22p^2\cdot 3s$	
$3s^4P_{2\frac{1}{2}}$	33979.0	$3s^2P_{1\frac{1}{2}}$	31156.0
$3s^4P_{1\frac{1}{2}}$	34025.7	$3s^2P_{\frac{1}{2}}$	31239.1
$3s^4P_{\frac{1}{2}}$	34059.5	$(^1D)3s^2D_{2\frac{1}{2},1\frac{1}{2}}$	17701?
		$2s^22p^2\cdot 4s$	
$4s^4P_{2\frac{1}{2}}$	13608.2**	$4s^2P_{1\frac{1}{2}}$	13154.9**
$4s^4P_{1\frac{1}{2}}$	13676.9**	$4s^2P_{\frac{1}{2}}$	13232.3**
$4s^4P_{\frac{1}{2}}$	13726.9**		
		$2s^22p^2\cdot 5s$	
$5s^4P_{2\frac{1}{2}}$	7417.1	$5s^2P_{1\frac{1}{2}}$	7264
$5s^4P_{1\frac{1}{2}}$	7487.2	$5s^2P_{\frac{1}{2}}$	7340
$5s^4P_{\frac{1}{2}}$	7531.5		
		$2s^22p^2\cdot 6s$	
$6s^4P_{2\frac{1}{2}}$	4662.4	$6s^2P_{1\frac{1}{2}}$	4554
$6s^4P_{1\frac{1}{2}}$	4734.4		
$6s^4P_{\frac{1}{2}}$	4779.1		
		$2s^22p^2\cdot 7s$	
$7s^4P_{2\frac{1}{2}}$	3198.5**	$7s^2P_{1\frac{1}{2}}$	3183
		$2s^22p^2\cdot 3p$	
$3p^4S_{1\frac{1}{2}}$	20593.3	$3p^2S_{\frac{1}{2}}$	23794.7* *a*
$3p^4P_{2\frac{1}{2}}$	21811.8	$3p^2P_{1\frac{1}{2}}$	19571.2
$3p^4P_{1\frac{1}{2}}$	21850.1	$3p^2P_{\frac{1}{2}}$	19606.9
$3p^4P_{\frac{1}{2}}$	21868.5		
		$3p^2D_{2\frac{1}{2}}$	20512.8*
$3p^4D_{3\frac{1}{2}}$	22461.9	$3p^2D_{1\frac{1}{2}}$	20588.8*
$3p^4D_{2\frac{1}{2}}$	22512.9		
$3p^4D_{1\frac{1}{2}}$	22550.2	$(^1D)3p^2P_{1\frac{1}{2}}$	5056.2
$3p^4D_{\frac{1}{2}}$	22572.8	$(^1D)3p^2P_{\frac{1}{2}}$	5082.2
		$(^1D)3p^2D_{2\frac{1}{2}}$	6831.6
		$(^1D)3p^2D_{1\frac{1}{2}}$	6855.1

		$2s^22p^2\cdot 4p$	
$4p^4S_{1\frac{1}{2}}$	9897.8*	$4p^2S_{\frac{1}{2}}$	10898.4
$4p^4P_{2\frac{1}{2}}$	10306.0*		
$4p^4P_{1\frac{1}{2}}$	10346.7*		
$4p^4P_{\frac{1}{2}}$	10362.3*		
$4p^4D_{3\frac{1}{2}}$	10474.3*		
$4p^4D_{2\frac{1}{2}}$	10528.9*		
$4p^4D_{1\frac{1}{2}}$	10564.9*		
$4p^4D_{\frac{1}{2}}$	10584.5*		
		$2s^22p^2\cdot 3d$	
$3d^4P_{2\frac{1}{2}}$	12388	$3d^2P_{1\frac{1}{2}}$	12761.6**
$3d^4P_{1\frac{1}{2}}$	12455 *b*	$3d^2P_{\frac{1}{2}}$	12722.1**
$3d^4P_{\frac{1}{2}}$	12481		
		$3d^2D_{2\frac{1}{2}}$	12232.7**
$3d^4D_{3\frac{1}{2}}$	12325.5*	$3d^2D_{1\frac{1}{2}}$	12256.2**
$3d^4D_{2\frac{1}{2}}$	12334.3*c		
		$3d^2F_{3\frac{1}{2}}$	12494.3**
$3d^4F_{4\frac{1}{2}}$	12577 ?*	$3d^2F_{2\frac{1}{2}}$	12566.1**
$3d^4F_{3\frac{1}{2}}$	12626.5?*		
$3d^4F_{2\frac{1}{2}}$	12660.8?*d		
$3d^4F_{1\frac{1}{2}}$	12688?*		
		$2s^22p^2\cdot 4d$	
$4d^4P_{2\frac{1}{2}}$	6942.2**	$4d^2P_{1\frac{1}{2}}$	7156.2*
$4d^4P_{1\frac{1}{2}}$	6994?*e*	$4d^2P_{\frac{1}{2}}$	7131.2**g*
$4d^4P_{\frac{1}{2}}$	7020.3**		
$4d^4D_{3\frac{1}{2}}$	7006.3?*	$4d^2F_{3\frac{1}{2}}$	7004
$4d^4D_{2\frac{1}{2}}$	7057.2*e*	$4d^2F_{2\frac{1}{2}}$	7066
$4d^4D_{1\frac{1}{2}}$	7069.5		
$4d^4D_{\frac{1}{2}}$	7123.6		
$4d^4F_{4\frac{1}{2}}$	7040.6		
$4d^4F_{3\frac{1}{2}}$	7096.6		
$4d^4F_{2\frac{1}{2}}$	7131.3		
$4d^4F_{1\frac{1}{2}}$	7149.1		
		$2s^22p^2\cdot 5d$	
$5d^4P_{2\frac{1}{2}}$	4433.1**	$5d^2P_{1\frac{1}{2}}$	4575.5*
$5d^4P_{1\frac{1}{2}}$	4471		
		$5d^2F_{3\frac{1}{2}}$	4472
$5d^4D_{2\frac{1}{2}}$	4520		
$5d^4F_{4\frac{1}{2}}$	4482.5*f		
$5d^4F_{3\frac{1}{2}}$	4546.4*		
		$2s^22p^2\cdot 6d$	
$6d^4P_{2\frac{1}{2}}$	3070.8**	$6d^2F_{3\frac{1}{2}}$	3096
$6d^4D_{2\frac{1}{2}}$	3157		
		$2s^22p^2\cdot 7d$	
$7d^4P_{2\frac{1}{2}}$	2242		

* New term.
** Value revised.

In several cases terms have been assigned to different configurations. from those chosen by previous authors. Kiess found high ^2P and ^2D terms at about 5100 and 6800 respectively. His work was done before the Hund

theory so, of course, he made no attempt to assign these to configurations. Hund[9] suggested that the ^2P term belonged to the $2s^22p^2 \cdot 5p$ configuration, thus being the third member of the series headed by $2s^22p^2 \cdot 3p\,^2P$, the second member of the series being unidentified. Compton and Boyce have followed him in this and in addition have assigned the ^2D term to $2s^22p^2 \cdot 4p$. These assignments appear untenable for the following reasons: (1) Two members of the series of ^4S ^4P ^4D and ^2S terms of these configurations have now been found and all follow a Rydberg formula rather closely whereas on the above assumption the series of ^2P and ^2D terms would show large deviations from such a formula; (2) there is no possible choice among the unidentified lines for the missing second member of the series; and (3) the separation of the ^2D term is only about one-third of that which would be expected. In this paper these terms have been assigned to the $2s^22p^2 \cdot 3p$ configuration but are considered as based on the ^1D term of the N II ion. The justification for this is as follows: The ^1D ^3P separation in N II is very well known to be 15100 wave-numbers. In fact this transition is directly observed in the two red nebular lines.[10] In the N I spectrum we expect a system of doublet terms based on the ^1D state of N II but these terms will be displaced to about 15000 units higher than the quartet and doublet terms of the same configurations which are based on the ^3P state. The terms of the $2s^22p^2 \cdot 3p$ configuration based on ^3P lie around 21000. Hence we should expect ^2P ^2D and ^2F based on ^1D near 6000. The ^2F is not found, doubtless because it does not combine strongly with any known terms to give lines in a region favorable for observation. It is to be noted that the ^2D term here is regular while the corresponding term in O II is inverted.

Compton and Boyce found an inverted ^2P term at about 17700 and assigned it to the $2s2p^4$ configuration. The corresponding term has been found by Bowen[3] in O II and F III combining with both the ^2P and ^2D terms of the ground configuration. Prediction by means of the irregular doublet law shows that this term in N I must lie high above the ^3P series limit at about -40000 and hence the previous assignment cannot be correct. There seems to be considerable doubt about the reality of the term observed by Compton and Boyce. The member of inner quantum number $\frac{1}{2}$ is identified on the basis of one combination only while that of inner quantum number $1\frac{1}{2}$ is fixed by only two lines whose separation differs by about 14 wave-numbers from that expected. Reasoning similar to that of the above paragraph predicts the $2s^22p^2(^1D)3s\,^2D$ term at 17500. By analogy with O II the separation should be too small to be resolved. The term at 17701 has been given this designation in the table but is marked as questionable.

Certain terms in Table I require some special discussion which will be given in a series of notes. The letters agree with those placed beside the terms in question in the table.

a. The $3p\,^2S$ term lies below any of the other terms of the $2s^22p^2 \cdot 3p$ configuration as is the case in O II. This is also true for the second member of the series.

[9] Hund, Linienspektren und Periodisches System der Elemente, p. 197 (1925).

[10] Bowen, Astrophys. J. **67**, 1 (1928).

b. The $3d^4P$ term should combine strongly with $3p^4S_{1\frac{1}{2}}$ but the lines predicted from the term values of Compton and Boyce fall so close to other strong lines that it cannot be said with certainty whether the infra-red data confirm this assignment or not. The values of Compton and Boyce have therefore been taken over without change.

c. This does not agree with the $3d^4D_{2\frac{1}{2}}$ term found by Compton and Boyce but their assignment was on the basis of one combination only. The $D_{1\frac{1}{2}}$ and $D_{\frac{1}{2}}$ members are not found from the infra-red data because the multiplet $3p^4P$—$3d^4D$ is only partially resolved and only the two strongest lines of $3p^4D$—$3d^4D$ can be detected.

d. $3d^4F$ would be expected to combine strongly only with $3p^4D$. After the rest of the spectrum had been analyzed only one group of lines, which lay at 10100A, could reasonably be given this designation. Predictions either from the analogous terms of O II or from higher members of the same series in N I suggested that, considering the low resolution obtainable in this region, the four diagonal members of the multiplet would probably be fused into one line. The line at 10113.4A was identified on this basis. Two other weaker lines fit in nicely for the $D_{3\frac{1}{2}}F_{3\frac{1}{2}}$ and $D_{2\frac{1}{2}}F_{2\frac{1}{2}}$ members so that the assignment seems to be fairly certain. Fowler and Selwyn have observed this strong line photographically but again under low dispersion. They gave it a designation as a member of the singlet system in C I but the assignment was unconfirmed by other combinations and was only tentative.

e. Kiess found a level at 6942 which he called $^4D_{3\frac{1}{2}}$. Compton and Boyce found a level at 6946 combining with $2p^4S_{1\frac{1}{2}}$ which is doubtless $4d^4P_{2\frac{1}{2}}$. Since there can easily be an error of 4 units in their term values it seems probable that the two levels are in reality the same one, $4d^4P_{2\frac{1}{2}}$. A strong pair of lines having the $3p^4P_{2\frac{1}{2}}D_{3\frac{1}{2}}$ separation determines a new term at 7006 which is probably the $4d^4D_{3\frac{1}{2}}$ term. The $4d^4P_{2\frac{1}{2}}$ and $P_{\frac{1}{2}}$ levels determined by Compton and Boyce give the expected combinations with $3p^4P$ and ^4D but the expected lines from their $4d^4P_{1\frac{1}{2}}$ term are missing. This term has therefore been denoted as questionable. No other satisfactory one has been found to replace it, however. Kiess's values for the $4d^4D_{1\frac{1}{2}}$ and $D_{\frac{1}{2}}$ terms are here interchanged. The former assignment made the $4d^4D$ term partially inverted while here it is regular. The intensities are in favor of the present designation.

f. Two strong unidentified lines fall close together at the position where the $3p^4D-5d^4F$ multiplet must lie. These have been assumed as $^4D_{3\frac{1}{2}}-{}^4F_{4\frac{1}{2}}$ and $^4D_{2\frac{1}{2}}-{}^4F_{3\frac{1}{2}}$ and used to fix the $5d^4F_{4\frac{1}{2}}$ and $F_{3\frac{1}{2}}$ levels. As they give very satisfactory values for these levels the assumption is probably justified.

g. Two strong outstanding lines at 6000A are doubtless $3p^2S-4d^2P$ since they give the expected separation and position for the $4d^2P$ terms and cannot otherwise be accounted for.

Spectrum of Carbon I

Table II gives those terms in the spectrum of carbon I which have been newly determined or revised in the present work. Term values are expressed relative to the triplet terms of Fowler and Selwyn. Those which are new are marked with an asterisk. The following notes discuss these terms:

a. The P_2 member of the $4s^3P$ term is very certain since it gives four combinations in the infra-red and two in the extreme ultra-violet. The P_1 and P_0 members depend upon only two lines each and are therefore less certain.

b. This $3p^3S_1$ term was found by Fowler and Selwyn but was marked as questionable since it depended on only two combinations. The infra-red combinations render the assignment quite certain.

c. It has not been possible to fix the $3d^3D_1$ level. The $3p^3P_0 - 3d^3D_1$ line which must be strong is probably masked by one of the other strong lines of the multiplet.

d. The $3p^3D - 3d^3F$ multiplet which is used to fix the $3d^3F$ levels is not fully resolved and the terms have therefore been indicated as questionable. The identification is very probably correct because this multiplet must contain the strongest lines in this region and no other choice remains among the unclassified lines.

TABLE II. *Term values in carbon I.*

$2s^22p \cdot 4s$			$2s^22p \cdot 3d$		
$4s^3P_2$	12869.7*		$3d^3P_2$	11706.9	
$4s^3P_1$	12901.1*	*a*	$3d^3P_1$	11700.6	
$4s^3P_0$	12924*		$3d^3P_0$	11694.9	
$2s^22p \cdot 3p$			$3d^3D_3$	12699.5	
$3p^3S_1$	20274.5	*b*	$3d^3D_2$	12710.7	*c*
$3p^3D_3$	21274.3*		$3d^3F_4$	12768.8?*	
$3p^3D_2$	21308.0*		$3d^3F_3$	12803.3?*	*d*
$3p^3D_1$	21329.2*		$3d^3F_2$	12819.0?*	

* New terms. Others are revised values.

Fowler and Selwyn determined the triplet term values for C I by an indirect method, adjusting the absolute values until the singlets and triplets had the same relative positions as in N II and O III. The present work fixes the second member of the series of s^3P terms. Extrapolation to the limit by means of a Rydberg formula applied to the $3s^3P_0$ and $4s^3P_0$ terms gives values some 300 units greater than those of Fowler and Selwyn. As this quantity is within the limit of error of such an extrapolation the values of these authors may be considered confirmed.

CLASSIFIED LINES

Table III gives a complete list of the lines observed in the infra-red region. The list of lines classified in the visible region is contained in the preceding paper by Duffendack and Wolfe. It will be seen that practically all the infra-red lines out as far as 16000A are accounted for. A few strong isolated lines are left and some of these probably belong to the singlets of C I. However it has not been possible to make any classification of the singlets with certainty. A group of rather weak lines between 5000 and 6000 wave-numbers remain unaccounted for. The terms of the *3d* configurations in both carbon I

TABLE III. *Classified lines in the infra-red region.*

Int.	I.A. Air	ν	Carbon I	Nitrogen I
50	9028.9	11072.5		$3p^2S_{\frac{1}{2}} - 3d^2P_{\frac{1}{2}}$
150	9045.1	11052.7		
350	9060.6	11033.8	$3s^3P_1 - 3p^3P_2$* $3s^3P_0 - 3p^3P_1$*	$3p^2S_{\frac{1}{2}} - 3d^2P_{1\frac{1}{2}}$
150	9077.8	11012.8	$3s^3P_1 - 3p^3P_1$*	
200	9088.4	11000.0	$3s^3P_1 - 3p^3P_0$*	
500	9094.7	10992.4	$3s^3P_2 - 3p^3P_2$*	
150	9111.0	10972.7	$3s^3P_2 - 3p^3P_1$*	
250	9263.7	10791.9	Oxygen I	
200	9386.5	10650.7		$3s^3P_{\frac{1}{2}} - 3p^3D_{1\frac{1}{2}}$
350	9392.5	10644.0		$3s^3P_{1\frac{1}{2}} - 3p^3D_{2\frac{1}{2}}$
300	9405.3	10629.4		
25	9460.0	10567.9		$3s^3P_{1\frac{1}{2}} - 3p^3D_{1\frac{1}{2}}$
60	9602.8	10410.8	$3s^3P_0 - 3p^3S_1$	
125	9620.4	10391.7	$3s^3P_1 - 3p^3S_1$*	
250	9657.5	10351.8	$3s^3P_2 - 3p^3S_1$*	
10	9821.8	10178.6		$3p^4D_{2\frac{1}{2}} - 3d^4D_{2\frac{1}{2}}$
60	9862.5	10136.6		$3p^4D_{3\frac{1}{2}} - 3d^4D_{3\frac{1}{2}}$
900	10113.4	9885.1		$3p^4D_{3\frac{1}{2}} - 3d^4F_{4\frac{1}{2}}$? $3p^4D_{2\frac{1}{2}} - 3d^4F_{3\frac{1}{2}}$? $3p^4D_{1\frac{1}{2}} - 3d^4F_{2\frac{1}{2}}$? $3p^4D_{\frac{1}{2}} - 3d^4F_{1\frac{1}{2}}$?
40	10147.3	9852.1		$3p^4D_{2\frac{1}{2}} - 3d^4F_{2\frac{1}{2}}$?
30	10164.5	9835.4		$3p^4D_{3\frac{1}{2}} - 3d^4F_{3\frac{1}{2}}$?
70	10506.5	9515.4		$3p^4P_{1\frac{1}{2}} - 3d^4D_{2\frac{1}{2}}$
60	10513.0	9509.5		$3p^4P - 3d^4D$ partially resolved
60	10521.0	9502.3		
60	10532.5	9491.9		
125	10539.0	9486.0		$3p^4P_{2\frac{1}{2}} - 3d^4D_{3\frac{1}{2}}$
60	10548.0	9478.0		$3p^4P_{2\frac{1}{2}} - 3d^4D_{2\frac{1}{2}}$
30	10591.8	9438.8		
8	10623.3	9410.8		
50	10653.6	9384.0		
500	10683.0	9358.2	$3s^3P_1 - 3p^3D_2$ $3s^3P_0 - 3p^3D_1$	
600	10690.5	9351.6	$3s^3P_2 - 3p^3D_3$	
100	10707.5	9336.8	$3s^3P_1 - 3p^3D_1$	
125	10729.2	9317.9	$3s^3P_2 - 3p^3D_2$	
12	10758.2	9292.8	$3s^3P_2 - 3p^3D_1$?	
10	11227.5	8904.2		$3p^4D_{2\frac{1}{2}} - 4s^4P_{2\frac{1}{2}}$
150	11286.5	8857.7	Oxygen I	
125	11294.0	8851.8	Oxygen I	$3p^4D_{3\frac{1}{2}} - 4s^4P_{2\frac{1}{2}}$
30	11313.8	8836.3		$3p^4D_{2\frac{1}{2}} - 4s^4P_{1\frac{1}{2}}$
200	11329.0	8824.5		$3p^4D_{1\frac{1}{2}} - 4s^4P_{\frac{1}{2}}$ Too strong
50	11564.8	8644.6		$sp^4\,{}^4P_{2\frac{1}{2}} - 3p^4S_{1\frac{1}{2}}$
30	11619.0	8604.3		
80	11628.0	8597.6		$sp^4\,{}^4P_{1\frac{1}{2}} - 3p^4S_{1\frac{1}{2}}$
100	11652.5	8579.6	$3p^3S_1 - 3d^3P_0$	
200	11656.0	8577.0	$3p^3S_1 - 3d^3P_1$	$sp^4\,{}^4P_{\frac{1}{2}} - 3p^4S_{1\frac{1}{2}}$
100	11667.1	8568.8	$3p^3S_1 - 3d^3P_2$	
100	11688.5	8553.1	Potassium I	
300	11747.5	8510.2	$3p^3D_1 - 3d^3F_2$?	
600	11754.0	8505.5	$3p^3D_3 - 3d^3F_4$? $3p^3D_2 - 3d^3F_3$?	
150	11770.6	8493.5	Potassium I	
10	11801.8	8471.0	$3p^3D_3 - 3d^3F_3$?	
10	11849.3	8437.1	$3p^3D_2 - 4s^3P_2$	
15	11863.0	8427.4	$3p^3D_1 - 4s^3P_1$	
15	11880.4	8415.0		

* Identified by Fowler and Selwyn.

TABLE III. (Continued)

Int.	I.A. Air	ν	Carbon I	Nitrogen I
200	11894.9	8404.8	$3p^3D_3-4s^3P_2$ $3p^3D_2-4s^3P_1$ $3p^3D_1-4s^3P_0$?	
30	11997.9	8332.6		$3p^2D_{1\frac{1}{2}}-3d^2D_{1\frac{1}{2}}$
60	12074.1	8279.8		$3p^2D_{2\frac{1}{2}}-3d^2D_{2\frac{1}{2}}$
10	12107.4	8257.2		$3p^2D_{2\frac{1}{2}}-3d^2D_{1\frac{1}{2}}$
20	12128.6	8242.7		$3p^4P_{1\frac{1}{2}}-4s^4P_{2\frac{1}{2}}$
100	12186.9	8203.2		$3p^4P_{2\frac{1}{2}}-4s^4P_{2\frac{1}{2}}$ $3p^4S_{1\frac{1}{2}}-3d^4P_{2\frac{1}{2}}$?
75	12203.4	8192.1		$3p^4P_{\frac{1}{2}}-4s^4P_{1\frac{1}{2}}$
8	12232.9	8172.4		$3p^4P_{1\frac{1}{2}}-4s^4P_{1\frac{1}{2}}$
75	12288.0	8135.8		$3p^4P_{2\frac{1}{2}}-4s^4P_{1\frac{1}{2}}$ $3p^4S_{1\frac{1}{2}}-3d^4P_{1\frac{1}{2}}$?
150	12327.7	8109.6		$3p^4S_{1\frac{1}{2}}-3d^4P_{\frac{1}{2}}$? Too strong
175	12380.3	8075.1		
20	12403.1	8060.3		
40	12437.7	8037.9	Potassium I	
200	12461.2	8022.7		$3p^2D_{1\frac{1}{2}}-3d^2F_{2\frac{1}{2}}$
350	12467.8	8018.5		$3p^2D_{2\frac{1}{2}}-3d^2F_{2\frac{1}{2}}$
30	12521.0	7984.4	Potassium I	
50	12551.0	7965.3	$3p^3P_0-3d^3P_1$	
30	12565.0	7956.5	$3p^3P_1-3d^3P_1$ $3p^3P_1-3d^3P_0$	
40	12582.3	7945.5	$3p^3P_1-3d^3P_2$	$3p^2D_{2\frac{1}{2}}-3d^2F_{2\frac{1}{2}}$
40	12602.6	7932.7	$3p^3P_2-3d^3P_1$	
200	12614.8	7925.1	$3p^3P_2-3d^3P_2$	
10	12898.2	7751.0		$3p^2D_{2\frac{1}{2}}-3d^2P_{1\frac{1}{2}}$
100	13164.1	7594.3	Oxygen I	
60	13426.1	7446.1		$3s^2P_{\frac{1}{2}}-3p^2S_{\frac{1}{2}}$
25	13462.3	7425.5		$sp^4{}^4P_{2\frac{1}{2}}-3p^4P_{2\frac{1}{2}}$
100	13500.2	7405.3	$3p^3S_1-4s^3P_2$	
60	13557.5	7374.0	$3p^3S_1-4s^3P_1$	
200	13578.8	7362.4		$3s^2P_{1\frac{1}{2}}-3p^2S_{\frac{1}{2}}$
100	13601.6	7350.1		$3p^2P_{\frac{1}{2}}-3d^2D_{1\frac{1}{2}}$
200	13622.9	7338.6		$3p^2P_{1\frac{1}{2}}-3d^2D_{2\frac{1}{2}}$
10	13649.3	7324.4		$sp^4{}^4P_{1\frac{1}{2}}-3p^4P_{\frac{1}{2}}$ $sp^4{}^4P_{\frac{1}{2}}-3p^4P_{1\frac{1}{2}}$
15	13666.6	7315.1		$3p^2P_{1\frac{1}{2}}-3d^2D_{1\frac{1}{2}}$
10	13696.5	7299.2	$sp^2{}^3D_3-3p^3P_2$	
5	13742.3	7274.8	$sp^2{}^3D_2-3p^3P_1$	
15	14313.0	6984.7		$3p^4S_{1\frac{1}{2}}-4s^4P_{2\frac{1}{2}}$
300	14399.6	6942.7	$3p^3P_1-3d^3D_2$	
500	14418.2	6933.7	$3p^3P_2-3d^3D_3$	
60	14441.1	6922.8	$3p^3P_2-3d^3D_2$	
40	14520.8	6884.8		$3p^2P_{\frac{1}{2}}-3d^2P_{\frac{1}{2}}$
400	14540.2	6875.6		
10	14559.6	6866.4		$3p^4S_{1\frac{1}{2}}-4s^4P_{\frac{1}{2}}$
8	14599.2	6847.8		$3p^2P_{1\frac{1}{2}}-3d^2P_{\frac{1}{2}}$ $3p^2P_{\frac{1}{2}}-3d^2P_{1\frac{1}{2}}$
5	14631.5	6832.7		
20	14681.1	6809.6		$3p^2P_{1\frac{1}{2}}-3d^2P_{1\frac{1}{2}}$
125	14755.7	6775.2		$sp^4{}^4P_{2\frac{1}{2}}-3p^4D_{3\frac{1}{2}}$
10	14779.8	6764.2	$3p^3P_2-4s^3P_2$	
5	14866.5	6724.7		$sp^4{}^4P_{2\frac{1}{2}}-3p^4D_{2\frac{1}{2}}$
25	14965.4	6680.3		$sp^4{}^4P_{1\frac{1}{2}}-3p^4D_{2\frac{1}{2}}$
10	15050.1	6642.6		$sp^4{}^4P_{1\frac{1}{2}}-3p^4D_{1\frac{1}{2}}$
10	15092.8	6623.8		$sp^4{}^4P_{\frac{1}{2}}-3p^4D_{1\frac{1}{2}}$
10	15145.7	6600.7		$sp^4{}^4P_{\frac{1}{2}}-3p^4D_{\frac{1}{2}}$
10	15161.1	6594.0		
6	15493.5	6452.6		$3p^2P_{\frac{1}{2}}-4s^2P_{1\frac{1}{2}}$

TABLE III. (Continued)

Int.	I.A. Air	ν	Carbon I	Nitrogen I
10	15582.3	6415.8		$3p^3P_{1\frac{1}{2}} - 4s^3P_{1\frac{1}{2}}$
15	15683.8	6374.3		$3p^3P_{\frac{1}{2}} - 4s^3P_{\frac{1}{2}}$
10	15770.7	6339.2		$3p^3P_{1\frac{1}{2}} - 4s^3P_{\frac{1}{2}}$
20	17082.5	5852.3		
30	17324.1	5770.7		
50	17335.2	5767.0		
10	17504.9	5711.1		
5	17636.8	5668.4		
5	17764.8	5627.6		
20	17820.5	5610.0		
5	17916.4	5580.0		
30	18020.7	5547.6		
5	19575	5107.2		
10	19742	5064.1		
30	21193	4717.2		
4	21290	4695.7		
10	21514	4646.8		
4	22909	4364.0		

Extreme ultra-violet lines, wave-lengths by Fowler and Selwyn.

Int.	I.A. Vac.	ν	carbon I
2	1280.75	78079	$2p^3P_1 - 4s^3P_0$
3	1280.33	78105	$2p^3P_2 - 4s^3P_2$
1	1279.85	78134	$2p^3P_1 - 4s^3P_2$
2	1279.17	78176	$2p^3P_2 - 3d^3F_3$? $2p^3P_1 - 3d^3F_2$?

and nitrogen I lie between 12000 and 13000 while the $4f$ terms should be hydrogen-like and hence have values about 7000. This makes it probable that this group of lines is due to transitions from $4f$ to $3d$ states in both carbon and nitrogen. Considering the small number and the weakness of the lines in this group it is not surprising that it has not been possible to classify them.

I am greatly indebted to Professor H. M. Randall for the infra-red apparatus which he has placed at my disposal.

THE DENSITIES OF HYDROGEN SPECTRAL LINES AS A FUNCTION OF THE ELECTRONIC VELOCITY OF EXCITATION

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Abstract

The densities of the principal lines of the singlet and triplet systems of molecular hydrogen, as well as H_α, H_β and H_γ were measured for electronic velocities in the range 19 to 220 equivalent volts, the electron emission and the gas pressure being kept constant. The triplet lines have no maximum density in this range but seem to be approaching one slightly below 19 volts. All the singlet lines show a decided maximum of density between 30 and 35 volts. The densities of H_α, H_β and H_γ decrease very rapidly below 30 volts indicating that the number of dissociating collisions which produce an excited atom must be very small at 19 volts. The use of curves showing the variation in the ratio of the densities of singlet and triplet lines with voltage is suggested as a method for finding the mean electronic velocities in certain types of gaseous discharges.

Introduction

During the past few years, the writer has been interested in studying the variation in intensity of lines of the secondary spectrum of hydrogen under different conditions of excitation. At the end of nearly every experiment, the conclusion was reached that after all, the electronic velocity of excitation was the most important factor influencing changes of intensity. So in view of our most recent knowledge of the origin of lines in the secondary spectrum,[1,2] it seemed desirable to get direct evidence of the influence of the electronic velocity of excitation on their intensity, by keeping all other conditions constant.

In 1923 Hughes and Lowe[3] performed some experiments very similar to the one proposed here. However, they were interested primarily in the Balmer lines and their data on the lines of the secondary spectrum were more or less fragmentary. Their measurements were confined to electronic velocities in the range 29 to 110 equivalent volts. In as much as marked changes in the intensity of the lines of the secondary spectrum seem to occur around 30 volts, the writer hoped to depress this lower limit as far as possible. Moreover, it was thought that somewhat more accurate results might be obtained by use of an equipotential source of electrons rather than the strip filament used by them. Finally, the writer hoped to confirm certain differences in behavior of the lines of the singlet and triplet systems of molecular hydrogen, which seemed to be indicated by their results.

* National Research Fellow.

[1] O. W. Richardson and K. Das, Proc. Roy. Soc. **A122,** 688 (1929).

[2] O. W. Richardson and P. M. Davidson, Proc. Roy. Soc. **A123,** 54 (1929).

[3] A. L. Hughes and P. Lowe, Phys. Rev. **21,** 292 (1923).

Apparatus and Procedure

The experimental tube used is shown in Fig. 1. The observation chamber *a*, being essentially plate and grid in one, was semi-cylindrical in shape, approximately fitting the glass tube. The grid part was made of coarse nickel gauze (18×18 mesh of 18 mil wire) while the "plate" part was of fine gauze (60×60 mesh of 8 mil wire). Approximately 1 mm below the grid was the equipotential cathode *b*, backed by a semi-cylindrical sheet of nickel *c* which served as a shield and focusing cup for the electrons emitted by *b*. Both cathode and shield were held in place by springs *s*. The equipotential cathode[4] seemed to be simply an oxide coated nickel shell, having inside it a tungsten filament packed in alundum cement. Three wires were brought in through the ground joint, two of which furnished current to heat the cathode, while the third was connected to the shell of the cathode and the shield. Positive accelerating voltages were applied at *d*. Thus electrons emitted by the equipotential cathode were accelerated to the grid of the observation chamber and, passing through it into the field free space, produced radiation by col-

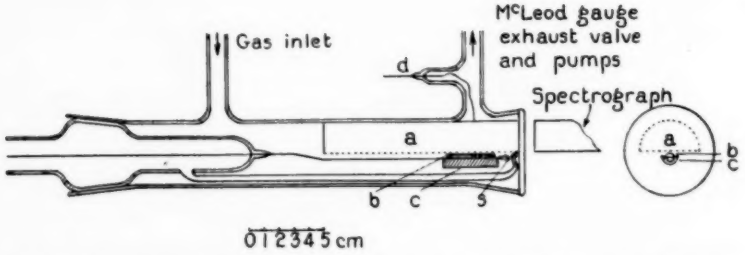

Fig. 1. Apparatus used to excite hydrogen by controlled electron impact.

lision with hydrogen molecules. This radiation was then photographed through an optical glass window sealed into the end of the tube.

Hydrogen was admitted to one end of the experimental tube by means of a platinum tube and was pumped out at the other end, thus insuring a continuous flow of pure hydrogen. The platinum tube was 20 cm long, 1 mm in diameter with 0.1 mm walls. It was surrounded by a glass jacket through which commercial hydrogen was flowed. On heating the platinum tube to a dull red heat (about 600°K) by passing a current of about 16 amperes through it, an adequate flow of hydrogen was obtained through the experimental tube. The pressure could be varied either by changing the temperature of the platinum tube or by means of a valve which regulated the rate of pumping. Pressures were measured by McLeod gauge.

The spectrograph used for photographing the radiation was a three prism Steinheil instrument having an opening $f/3.0$ and giving a dispersion of 113A per mm at H_α, 31.3A per mm at H_β and 13.5A per mm at H_γ. Ilford Special Rapid Panchromatic Plates were used for all exposures.

[4] This was obtained from Dr. M. J. Kelly of the Bell Telephone Laboratories through the kindness of Professor A. J. Dempster and Professor H. B. Lemon of this laboratory.

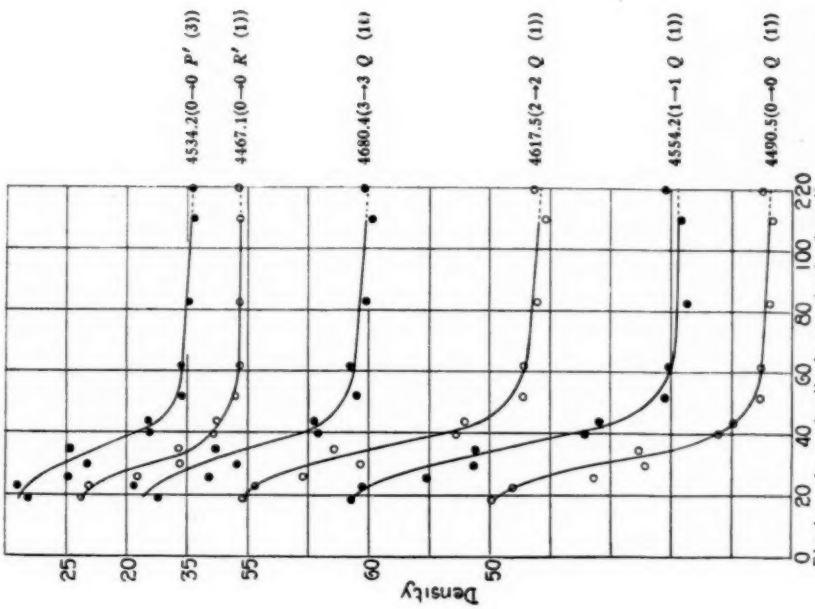

Fig. 3. Density-voltage curves for the $4^3\Pi \rightarrow 2^3\Sigma$ system.

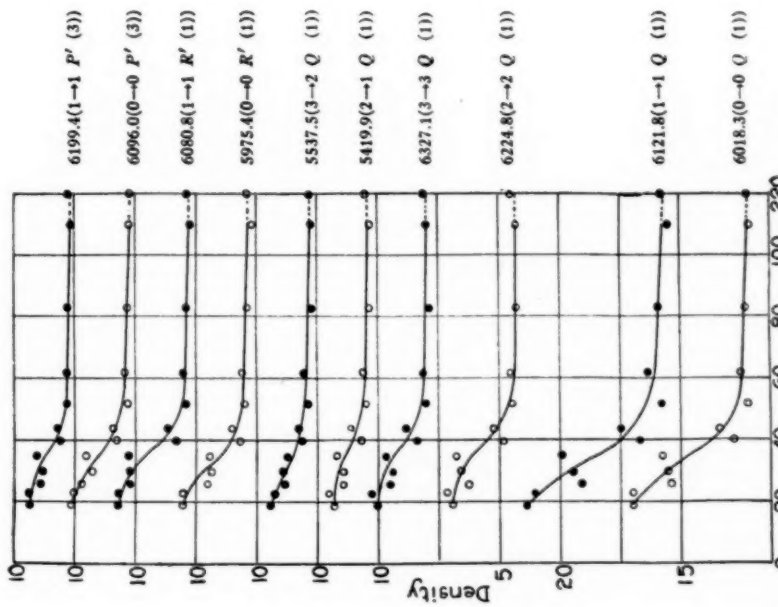

Fig. 2. Density-voltage curves for the $3^3\Pi \rightarrow 2^3\Sigma$ system.

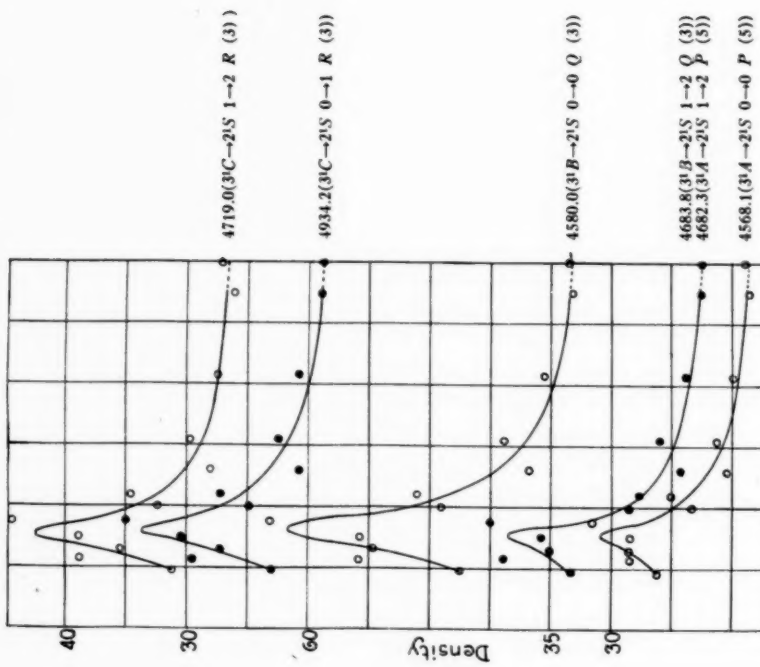

Fig. 5. Density-voltage curves for the singlet systems.

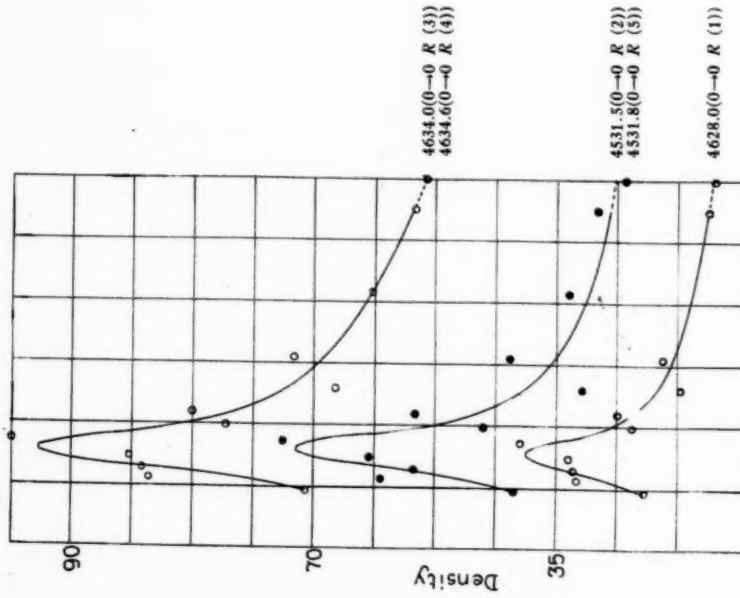

Fig. 4. Density-voltage curves for the $3^1C \rightarrow 2^1S$ system.

During all exposures the electron emission was kept constant at 20 milliamperes and the pressure constant at 0.03 mm. At this pressure, the electronic mean free path[5] in hydrogen is about 2 cm, so that the chance of an electron making more than one collision is very small. Two plates were taken on which all exposures were of one hour duration. On the first plate the accelerating voltages were 23, 35, 62, 110, 83, 44 and 30; on the second plate the voltages were 19, 26, 40, 52 and 220. Below 19 volts the radiation was too feeble to photograph successfully in one hour.

Microphotometric traces were then made of all the spectra by means of a Moll self-registering microphotometer. From these traces the density of any line could be obtained by use of the relation: density $= \log d/d - h$, where d is the total galvanometer deflection in the absence of a line and h is the height of the peak on the trace corresponding to the line. Curves were then plotted showing the variation of the density of a line with the electronic velocity in equivalent volts.

Results

The density-voltage curves for the principal lines of the triplet system of H_2 are shown in Figs. 2 and 3, and for the singlet system in Figs. 4 and 5. They are all plotted on the same scale and one density value is given for each curve. It will be noticed that densities at 23, 35 and 62 volts are uniformly high while densities at 26, 30, 40 and 52 volts are slightly low. In other words if photographs had been taken at constantly increasing voltages, the density values would probably have fallen on a smooth curve. But it is doubtful whether such a curve would have been as true a picture of conditions as the mean curve obtained by this method.

These density-voltage curves show that there is a decided difference in the behavior of singlet and triplet lines. The triplet lines have no maximum but seem to be approaching one slightly below 19 volts. On the other hand, all the singlet lines show a decided maximum of density between 30 and 35 volts. This, then, should be an excellent criterion for assigning an unknown line to either the singlet or triplet system. And, incidentally, it is also a nice confirmation of Richardson's analysis of the lines of the secondary spectrum.

The writer did not go to the trouble of calibrating the plates so that density values could be changed into intensity values, for after all, we are most interested in the voltages at which a maximum occurs and this should be the same for intensities as for densities. There are, however, two possible sources of error which might cause a shifting of the curves. In the first place, no account was taken of the distribution of velocities of the electrons going through the grid; the effect of this would probably be very small. However, the second source of error may be more serious. It will be remembered that it was the total electron emission to grid *and* plate which was kept constant, rather than the number of electrons penetrating through the grid. Thus if the ratio of the number penetrating through the grid to the total number collected varies appreciably with voltage, the result would be a shifting of the maxima to slightly lower voltages.

[5] Handbuch der Experimental Physik Vol. XIV, 192 et seq.

In Fig. 6 are shown the density-voltage curves for H_α, H_β and H_γ. The curves for the most intense lines of the singlet and triplet systems are also shown to give an idea of relative densities. As a matter of fact, H_α and H_β were really too intense on the photographic plates for an accurate measurement of density; for this reason the points at high densities fluctuated rather badly and only the mean curves are shown. The only reason for showing these curves is to indicate the rapid fall in density of H_α, H_β and H_γ at low voltages. From this we conclude that the number of dissociating collisions

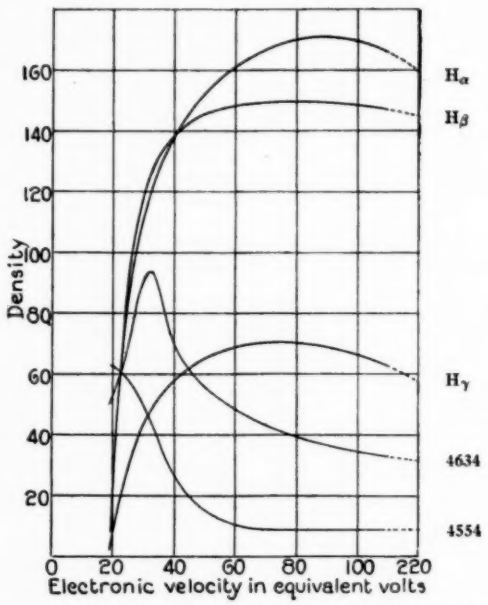

Fig. 6. Density-voltage curves for H_α, H_β and H_γ; also for the most intense lines of the singlet (4634) and triplet (4554) systems of H_2.

which produce an excited atom must be very small at 19 volts; for at these small electron currents there is little chance of an electron colliding directly with a hydrogen atom.

Discussion

It is interesting to see how the ratio of the densities of singlet and triplet lines vary with voltage. Four such curves are shown in Fig. 7. They are in accordance with Ornstein and Burger's selection principle[6] which states that at high electronic velocities, impacts causing transitions between singlet and triplet states are improbable in the same way that transitions between such states to produce radiation are improbable.

These curves have been obtained by finding the densities of certain lines at known voltages of excitation. The writer ventures to suggest that they might also be used to find the mean electronic velocity of excitation when the densities of the lines are known. For these curves are independent of the

[6] L. S. Ornstein, H. C. Burger and W. Kapuscinski, Zeits. f. Physik **51**, 45 (1928).

time of exposure and of the current density since both numerator and denominator of the ratio would be multiplied by the same factor. They are also independent of the kind of plate used for they are so close together that the change in sensitivity of the plate from one to the other would be inappreciable. Finally, Lowe's curves[7] giving the variation of intensity of secondary lines with pressure show that these curves should be independent of pressure for electron velocities above 35 volts; and they should hold at least qualitatively for voltages below this.

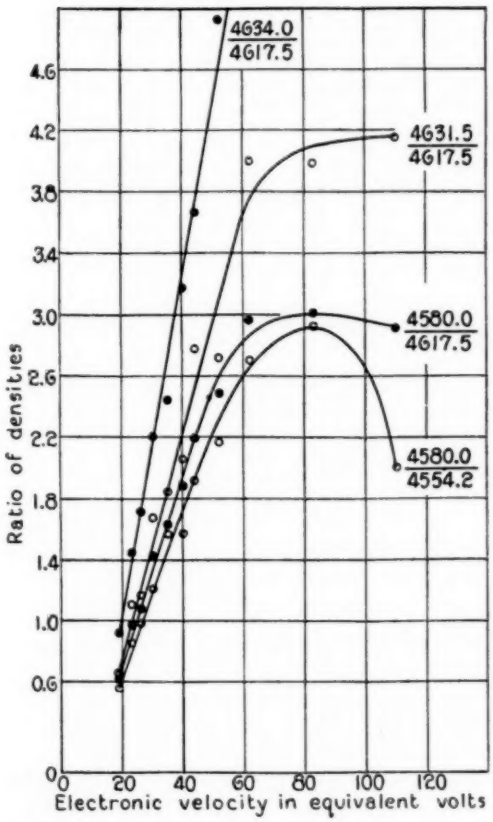

Fig. 7. Variation in the ratio of densities of singlet and triplet lines with the electronic velocity.

An example of such an application of these curves is the following. During the course of some work on an electrodeless ring discharge in hydrogen, the writer estimated that the mean electronic velocity was 15 volts at 0.08 mm pressure and greater than 30 volts at 0.0025 mm pressure. By use of the curves of Fig. 7 it now appears that these values should have been 30 and 36 volts respectively. It is in just such cases as the electrodeless discharge that the writer feels that the method outlined here would be more suitable for measuring electronic velocities than the exploring electrode method.

[7] P. Lowe, Trans. Roy. Soc. Can. **20**, 217 (1926).

INTENSITIES IN THE HARMONIC BAND OF HYDROGEN CHLORIDE

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Abstract

Measurement of absorption intensities.—The intensities of the first nine lines of the negative branch of the first harmonic absorption band of HCl at 1.76μ have been measured with a prism spectrograph, using a galvanometer and thermo-relay to observe thermopile voltages. The positive branch, not being resolvable, was measured as a whole. The areas under the lines in a plot of percent absorption against frequency were obtained for 5 different tube lengths, namely 74.5, 25.0, 14.96, 9.90 and 4.88 cm and the integrated absorption coefficient of each line was calculated from the slope of the curve of area against tube length at the origin by methods developed by Bourgin. The probable error of the intensity measurements for the stronger lines was 6 percent.

Correlation with theory.—A calculation is made of the intensity ratio of the band as a whole to that of the fundamental based on a solution of Schrödinger's equation obtained by Morse for an anharmonic oscillator, and the value so obtained is within 6 percent of the experimental value. A second order perturbation calculation based on harmonic oscillator functions did not give concordant results. An unpublished analysis of the effect of rotation on the relative intensities of the lines in a band by Kemble is given and the relative intensities calculated for this band, giving agreement with experiment within 5 percent.

Introduction

THE discovery of the harmonic band of HCl at 1.76μ by Brinsmade and Kemble[1] was of importance in establishing the fact that the HCl molecule behaves as an anharmonic oscillator and in showing how this was to be interpreted on the basis of the quantum theory. Since then the constants of the molecule have been determined from the frequencies of the band lines[2, 3] and, in particular, the anharmonicity of the oscillator has been determined from the discrepancy between the spacing of the centers of the different bands as observed and the spacing predicted by the "one, two, three" rule for harmonic frequencies which one would expect classically. The harmonic bands would be entirely absent in the spectrum of an ideal linear oscillator, so that the intensities of the different harmonic bands provide another means of measuring the departure from harmonicity.

The work on intensities of absorption bands in this region is very meager because most measurements, using only one length of absorption tube, do not give an accurate estimate of intensities except under particular circumstances (see below in the discussion of Dennison's work), and in order to get good results it is necessary to adopt the more tedious procedure of using a

[1] J. B. Brinsmade and E. C. Kemble, Proc. Nat. Acad. **3**, 420 (1917).

[2] E. S. Imes, Astrophys. J. **50**, 251 (1919).

[3] "Report on Molecular Spectra in Gases," Nat. Res. Council., No. 57, 1927 especially pp. 52–68. This will be referred to hereafter as "Report."

number of different tube lengths and calculating the absorption coefficients by a process involving extrapolation to zero length. Bourgin[4] has measured in this fashion the intensities of the lines of the absorption band at 3.46μ and this paper reports measurements on the first harmonic band at 1.76μ with essentially the same method and apparatus. The absorption of the first nine lines of the negative branch was measured for five different tube lengths, and their integrated absorption coefficient obtained by the methods developed by Bourgin[4], and in a similar fashion the intensity of the positive branch as a whole was measured. Owing to the fact that the positive branch was not sufficiently resolved to give reliable data for its component lines separately, the branch was treated as a whole. The theoretical intensities of the lines have also been calculated and agree satisfactorily with experiment.

Experimental Work

The spectrometer and thermopile were the same which Bourgin[4] used and were set up in the same fashion, except that a larger prism was used which measured 9.8 cm wide by 6.7 cm high. The prism angle was 60°. The wave-length range falling on a slit 0.04 mm wide was about 17A and for slits this wide, the resolving power, which was just insufficient to resolve the isotopic doublets (separated by 14A), was limited principally by the size of the prism.

The source was an ordinary tubular 250-watt projection-bulb of the type sold commercially for portable moving-picture projectors. The filament is arranged in six parallel strands, all in a vertical plane so that when looked at edgewise, it appears to be a narrow and very intense strip of light. The energy from this source, in the region of 1.76μ was about twice that of a Nernst glower and it had the added advantage of being simple to operate. The current was supplied by a motor generator run by a synchronous motor from the 550-volt mains, so that there was no trouble from fluctuating intensity of the source.

The absorption tubes were of glass, about 5 cm in diameter and of five different lengths, namely 74.05; 25.0; 14.96; 9.90; and 4.88 cm. The windows on the ends were of fused quartz, optically flat and about 1.5 mm thick. The light beam from the source passed through a focus in the tube so that the beam never acquired a diameter of more than 2 cm inside the tube, and, as the tubes were 5 cm in diameter, it was not necessary to insert diaphragms or to make other provisions to reduce reflections from the side walls.

The HCl was generated by dropping concentrated sulphuric acid on pure NaCl, and passing the gas through concentrated sulphuric acid to dry it before passing it into the absorption tube. Between the generator and the tube there was only one short length of rubber tubing, all the rest being glass and, as the gas was passed through rapidly, the chance of contamination by the rubber was slight. The exact correspondence of the curves obtained with those of other workers in this region [1, 2] was taken as evidence that the HCl was pure.

The thermopile was the same Coblentz, silver-bismuth, twenty-six junction thermopile which Bourgin used. It was enclosed in a glass tube which

[4] D. C. Bourgin, Phys. Rev. **29**, 794 (1927).

was evacuated by an ordinary "Cenco" pump. The current from the thermopile was observed by a thermo-relay manufactured by Kipp & Sons in Holland. The primary galvanometer, connected directly to the thermopile, was a Kipp instrument with a sensitivity of 1.2×10^{-9} amps. per mm and the secondary galvanometer (or observing galvanometer) was a Weston, gravity controlled, moving coil instrument with a sensitivity adjustable between 10^{-9} and 10^{-11} amps. per mm and ordinarily used in these experiments at a sensitivity a little below 10^{-10} amps. per mm. With these galvanometers the limit to the total sensitivity attainable with the relay was set by the Brownian movement[5] of the primary galvanometer which became noticeable at sensitivities of about 10^{-12} amps. per mm. The set was used just short of that point. It was found necessary to shield the entire primary galvanometer circuit against magnetic disturbances, as random magnetic fluctuations induced appreciable currents in the circuit. Zero-drift troubles were obviated by having the spectrometer and galvanometers in a separate room from the observer and source, and by thoroughly lagging the thermopile.

The absorption tubes were mounted on a rack which could be swung back and forth so that the tube was either in or out of the light path. A dummy tube, not filled with HCl though otherwise just like the others, was also mounted on the rack, so that when the filled tube was not in the light path the dummy was. For a given spectrometer setting the absorption was measured by rapidly interchanging the filled and dummy tubes and noting the resulting deflection of the galvanometer. This gives ΔI the amount of energy absorbed. The total intensity, I, of the beam could then be measured by closing a shutter in front of the entrance slit of the spectrometer while the dummy tube was in the beam, and the ratio $\Delta I/I$ gives the percent absorption. Inasmuch as there are no absorption bands of air, water vapor, or CO_2 in the region around 1.76μ of sufficient intensity to be observable, it was not considered necessary to evacuate the dummy tube. It was also assumed that there was no appreciable selective reflection from the tube windows.

The positions of the spectrometer were read from a dial on the end of a rod which was attached to the tangent screw of the spectrometer so that the table could be turned from the observers position in front of the galvanometer telescope. The readings of this dial could be calibrated in terms of frequency by two methods. One method was to calibrate the dial by the divided scale on the table and then go over to frequency by the usual formula for the dispersion of a prism, and the known refractive index of quartz in this region, and the other method was to compare the separation of the peaks of the lines in the negative branch in dial degrees with their frequency separation as given by Imes.[2] The mean of the results of these two methods was used.

Calculations

The absorption of light in a gas follows the exponential law so that if I_0 is the initial intensity of the beam and I the intensity after having passed through a certain length x of gas, then $I/I_0=e^{-\mu x}$, where μ is the coefficient of absorption. μ, of course, is a function of frequency. The intensity of a

[5] Ising, Phil. Mag. 1, 827 (1926).

line,[6,7] or the integrated absorption coefficient α, is defined by the equation $\alpha=\int_0^\infty \mu(\nu)d\nu$, the integral being taken over the line in question. The percent absorption for any given frequency is given by $(1-I/I_0)=1-e^{-\mu x}$ and the area, $A(x)$, under a line is given by $\int_0^\infty (1-e^{-\mu x})d\nu$, from which one can immediately verify that

$$\alpha=\left(\frac{dA}{dx}\right)_{x=0}=\int_0^\infty \mu(\nu)d\nu.$$

This explains the necessity of using a number of different tube lengths and calculating the areas under the lines in order to get the true intensity. Dennison[8] has developed a theory for calculating the relative absorption coeffcients of the lines in a band from observations on one tube length, but he assumes that the tube length is great enough that the absorption at the center of the line is nearly complete. To have fulfilled this condition for the harmonic band would have required impracticably long absorption tubes, since

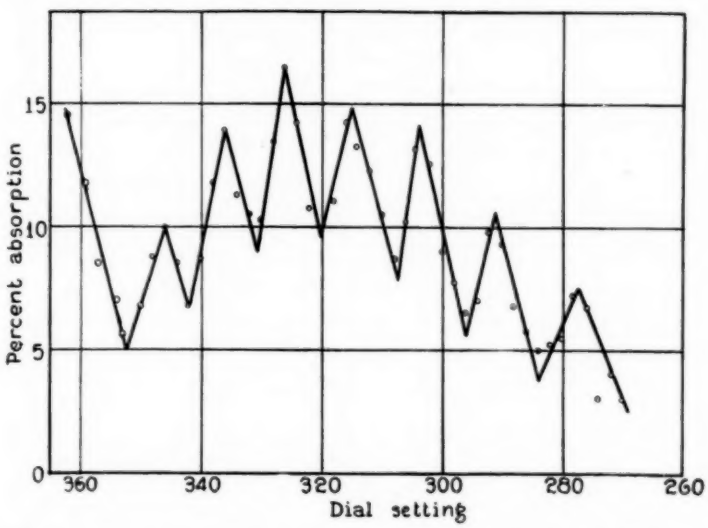

Fig. 1. Percent absorption plotted against spectrometer dial setting.

the greatest absorption for the 75 cm tube was only 31 percent. In his work there are also a number of special assumptions about line shape and slit width so that it is open to question whether his theory would give reliable results even if the absorption were sufficiently intense. Besides, Dennison's method, giving only relative coefficients for the lines in a band does not make it possible to use only one tube length if absolute intensities are desired.

The percent absorption was plotted against dial settings, of which a typical curve is shown in Fig. 1. In view of the closeness of the peaks it was decided to draw the best straight lines through the points on each side of a peak. The area could then be calculated by considering each line as a trapezoid superposed by a triangle. Of course the area under a line strictly

[6] R. C. Tolman, Phys. Rev. **23**, 693 (1924).
[7] E. C. Kemble, Phys. Rev. **25**, 1 (1925).
[8] Dennison, Phys. Rev. **31**, 511 (1928).

speaking extends over an infinite frequency range. However, it is a good approximation to assume that the line area is given by the area bounded by successive minima because, where the heights of successive peaks change linearly with frequency the net loss in area by overlapping is zero, and where the peak heights are not linear in frequency, the change in height is small enough that there would be no appreciable correction.

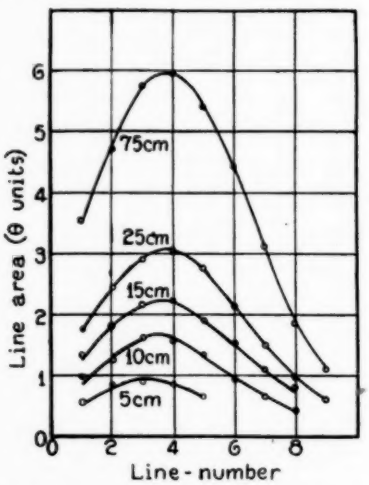

Fig. 2. Areas under absorption curves plotted as function of ordinal numbers of lines.

The areas determined were plotted as a function of ordinal number (Fig. 2), one plot to each tube length, and the best smooth curve drawn through the points. The areas of the various lines were then read from the smoothed curves, so that the area of a line was checked against that of its neighbors. In Table I are given the areas both "smoothed" and "un-

TABLE I. *Areas under absorption curves for tubes of various lengths. "O" heads columns of the original, "unsmoothed" areas; "S" heads columns of areas as read from "smoothing curves" of the type shown in Fig. 2.*

Line No.	75 cm		25 cm		15 cm		10 cm		5 cm	
	O	*S*	*O*	*S*	*O*	*S*	*O*	*S*	*O*	*S*
1	355	345	176	176	135	127	100	85	56	50
2	471	477	246	246	182	185	128	131	87	80
3	575	572	292	295	216	216	164	163	90	94
4	597	597	309	309	224	221	156	163	86	87
5	540	547	279	279	191	191	135	131	68	63
6	444	444	216	216	155	152	98	99		
7	318	318	150	150	113	109	67	68		
8	185	190	98	98	83	75	44	43		
9	113	113	63	63						

smoothed." These "smoothed" areas were plotted against tube length, one plot for each line of which Fig. 3 is a sample, and it was the slope of these lines at the origin that gave α.

Bourgin has developed two analytical methods for getting the slope of these curves at the origin, and they are superior to graphical or Taylor-series methods because they make greater use of the part of the curve lying at a distance from the origin in determining its slope at that point. That is to

say, they use *all* the data to derive α instead of depending largely on the two shortest tube lengths.

The first method[14] gives only the ratio of the α's of a given line to that of a standard line, and does not give the absolute value of α. The basic assump-

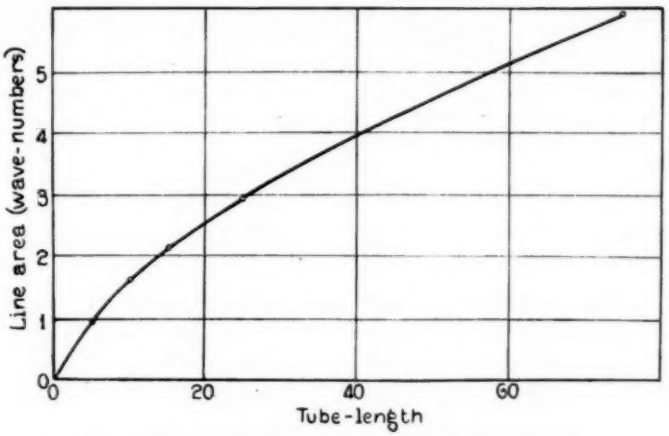

Fig. 3. "Smoothed" area as a function of tube length.

tion is that all the lines have approximately the same shape, though it is not necessary to specify what shape, and then it can be shown that if x'_m and $x'_{m'}$ are values of the abscissae for the given line (m) and the standard line (m') which have the *same ordinate*, then

$$\lim_{x_m \to 0} \frac{x'_{m'}}{x'_m} = \frac{\alpha_m}{\alpha_{m'}}.$$

Fig. 4 is a graph of $x'_{m'}/x'_m$ for the various lines referred to line 3 as a standard, and the extrapolation of the curves to the axis of ordinates is the

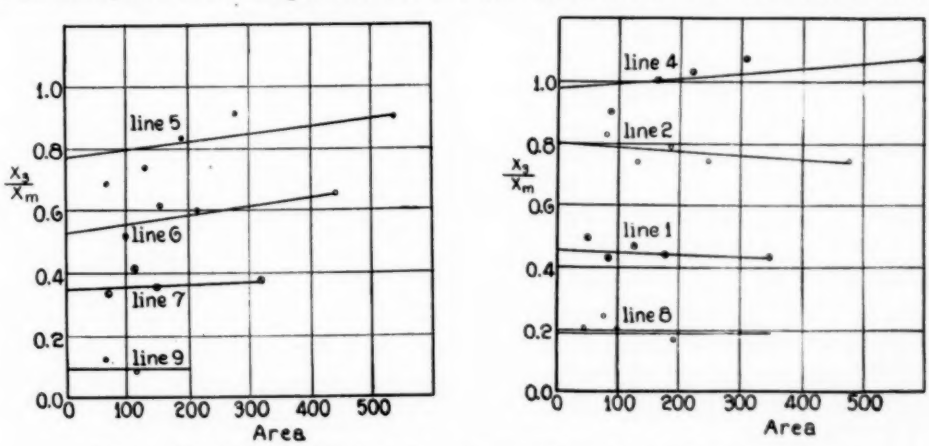

Fig. 4. Graph of $x'_{m'}/x'_m$ for various lines, referred to line 3 as a standard.

ratio of α_m to α_3. Bourgin discusses at some length the theoretical curvature of these curves on the assumption that the absorption lines are really close, unresolved, doublets, due to the existence of the two isotopes of chlorine,[9]

[9] F. W. Loomis, Astrophys. J. **52**, 248 (1920).

but for numerical values it is a good approximation to use straight lines. The relative values of the coefficients obtained in this manner are tabulated in Table II.

TABLE II. *Relative values of integrated absorption coefficient. α is in frequency units per centimeter tube length; b is in frequency units. Columns 2 and 3 are respectively, absolute and relative values as given by method II; Column 4 gives relative values as given by method I; Column 5 is weighted average of Columns 3 and 4.*

Line No.	$\alpha\times10^{-10}$	α_m/α_3	α_m/α_3	α_m/α_3	calc. ratio	A_m^2/A_3^2	$b\times10^{-10}$
		method II	method I	ave.			
1	0.329	0.494	0.468	0.485	0.501	0.360	1.37
2	0.574	0.862	0.796	0.840	0.859	0.696	1.42
3	0.666						1.146
4	0.620	0.931	0.961	0.941	0.942	1.087	1.92
5	0.500	0.751	0.737	0.746	0.755	0.914	1.99
6	0.348	0.522	0.521	0.522	0.503	0.603	
7	0.205	0.324	0.338	0.329	0.325	0.308	
8	0.118		0.177	0.177	0.181		
9	0.057		0.085	0.085	0.088		
R branch	4.14	6.21			5.91		

Bourgin's second method[10] assumes a definite shape for the lines, namely that $\mu=a/[(\nu-\nu_2)^2+b^2]$ where a and b are disposable constants and ν_1 is the frequency of the center of the line. Let $\psi(y)=\int_0^\infty(1-e^{-ay/(\nu^2+b^2)})d\nu$; then ψ is fitted to the experimental A by changing the scale of y and in this way a condition is obtained for a and b. From these, α is directly calculated by the simple expression $\alpha=\pi a/b$. The half-width of the line is b. The values of α and b obtained by this method are tabulated in Table II.

The positive branch was not resolved sufficiently to get individual line-areas from it, so the branch was measured as a whole and its absorption coefficient obtained graphically from a curve of the type shown in Fig. 4. This value is also given in Table II.

Dennison's work can be used, as already mentioned, to calculate the relative absorption coefficients of the lines in a band. He arrives at a formula (reference 8, p. 510) for the area under an absorption line, which is essentially $A^2=K\alpha x$ where K is a constant, and this shows at once that the approximations he used are not good at short tube lengths, since according to the formula, $(dA/dx)_{x=0}$ is infinite. For a given length of tube this formula indicates that α is proportional to A^2, so A^2_m/A^2_3 was calculated from the data on the 75 cm tube and the values are given in Table II. These, of course, should be the ratio of the intensities of the different lines in comparison to that of line 3, but the divergence from the relative intensities calculated by Bourgin's methods and from the theoretical intensity ratios is sometimes more than twenty percent, which means that Dennison's approximations are not good for bands of such small intensity as this one.

ACCURACY

There were two principal sources of error in the measurements. The first was the limit of precision to which the galvanometer could be read. The mean deviation from the mean of 75 galvanometer readings was 0.3 mm and

[10] D. C. Bourgin, Phys. Rev. **32**, 237 (1928). Bourgin assumes several specific shapes, but arrives at the conclusion that this one is the best.

this is 7 percent of the average galvanometer deflection (4 mm). Of course, for the stronger lines and the longer tubes, the percent error was somewhat less, and for the weak lines and the short tubes somewhat more. The fact that four readings were taken at each point makes the corresponding probable error in the determination of one point 3.5 percent.

The second main source of inaccuracy was a zero error. It was found that the deflection on exchanging tubes with the spectrometer set for a wavelength outside the band, was not zero and this residual deflection changed from time to time. It was impossible, on this account, to avoid an error of about 5 percent in the absorption values.

A consideration of the effect of these errors on the areas, the fact that each band was measured four times, and the effect of smoothing in increasing the accuracy, indicates that these two major sources of inaccuracy would give a probable error of 5 or 6 percent to the value of α for line 3. It is not to be expected that the less intense lines would have as high a degree of accuracy, but in view of the smoothing to which the data were subjected the error is not to be considered as being proportional to the faintness of a line.

Correlation with Theory

The first matter of interest in a discussion of the relation between the experimental data and the theoretical intensities is that of the intensity of the band as a whole. To find the theoretical intensity it is necessary to calculate the matrix component of the electric moment for the two vibrational states involved, namely the states 0 and 2, and to do this we must know the wave functions for these two states. Morse[11] has obtained an exact solution of Schrödinger's equation for an oscillator with a potential function composed of exponentials. The wave functions he obtains are to be preferred to those obtained by perturbation methods because with them the computation of intensities is less tedious. Morse has shown that his analysis gives the correct energy level formula, namely

$$E_n = h\nu_0(n+\tfrac{1}{2}) - h\nu_0 x(n+\tfrac{1}{2})^2 \tag{1}$$

where n is the vibrational quantum number; ν_0 is the frequency of a small classical vibration about the equilibrium point and x is the usual constant of anharmonicity, so these functions may be supposed to give correct intensity relations also.

The potential function which Morse introduces is

$$U(r) = D(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}) \tag{2}$$

where D is the energy of dissociation, r the nuclear separation, r_0 the equilibrium value of r and a a disposable constant. This function has a minimum at $r = r_0$, approaches zero asymptotically as r becomes infinite and has a very large value (not infinite) when $r = 0$. It is therefore of the correct general shape, and by a proper choice of D, a, and r_0 can be made to fit the data of any particular molecule quite well.

[11] P. M. Morse. To appear shortly. Dr. Morse kindly supplied Professor Kemble with a manuscript copy, which I have used.

Schrödinger's equation for the radial part of the wave function of a rotating oscillator may be thrown into the form

$$\frac{d^2R}{dr^2}-\frac{j(j+1)R}{r^2}+\frac{8\pi^2\mu}{h^2}(E-U)R=0 \tag{3}$$

where, if X is the radial part of Ψ, $R=rX$ and $\mu=m_1m_2/(m_1+m_2)$, is the ordinary mass coefficient. Morse has worked out the solution, R_n, if (2) is used for the potential function, and the term $j(j+1)R/r^2$ is omitted as being small (cf. below in the discussion of relative intensities). His solution is

$$R_n(r)=A_ne^{-(k/2)e^{-a(r-r_0)}}\left[ke^{-a(r-r_0)}\right]^{(k-2n-1)/2}L_{kn}(ke^{-a(r-r_0)}) \tag{4}$$

where $k=4\pi(2\mu D)^{1/2}/ah$ and $L_{kn}(ke^{-a(r-r_0)})$ is a polynomial in $(ke^{-a(r-r_0)})$, closely related to the generalized Laguerre polynomial and defined by

$$L_{kn}(x)=x^n-n(k-n-1)x^{n-1}+\tfrac{1}{2}n(n-1)(k-n-1)(k-n-2)x^{n-2}\cdots.$$

A_n is given by the formula

$$A_n=\left(\frac{a(k-2n-1)}{n!(k-n-1)\Gamma(k-n-1)}\right)^{1/2}.$$

The constants a and k appearing in (4) are related to the observable spectroscopic constants by the relations

$$a=(8\pi^2\mu c\nu_0x/h)^{1/2} \qquad\qquad k=1/x \tag{5}$$

where ν_0 is in wave-numbers and x is the anharmonicity constant appearing in the energy-level Eq. (1).

With these wave functions we are in a position to calculate the matrix component of the electric moment of the molecule for the transition $0\rightarrow2$. The electric moment $p(r)$ is a function of the nuclear separation and, for HCl, may be assumed to be linear in r within the range of r for which the wave functions are noticeably different from zero. So we can express $p(r)$ as $p(r_0)+(r-r_0)(dp/dr)_{r=r_0}$ or, if we let $(dp/dr)_{r=r_0}=p_0'$, $p(r)=p(r_0)+(r-r_0)p_0'$. The matrix component P_{nm} of p is given by $\int pR_nR_mdr$, and, if we change to the variable $u=r-r_0$, we have, due to the orthogonality of the R's

$$P_{nm}=p_0'\int_0^\infty uR_nR_mdu. \tag{6}$$

Substituting the values of R given in (4), one has

$$P_{02}=p_0'A_0A_2k^{k-3}\left\{k^2J_{k-1}-2k(k-3)J_{k-2}+(k-3)(k-4)J_{k-3}\right\} \tag{7}$$

where $J_{k-i}=\int_{-\infty}^{\infty}e^{-ke^{-au}}e^{-(k-i)au}udu$.

To evaluate these integrals one first makes the transformation $x=e^{-au}$ under which J becomes

$$J_{k-i}=-(1/a^2)\int_0^\infty e^{-kx}x^{k-i-1}\log x\,dx. \tag{8}$$

Inspection shows that (8) can be expressed as

$$J_{k-i}=\frac{1}{a^2}\frac{d}{di}\left(\int_0^\infty e^{-kx}x^{k-i-1}dx\right)=\frac{1}{a^2}\frac{d}{di}\left(\frac{\Gamma(k-i)}{k^{k-i}}\right) \tag{9}$$

$$=\frac{1}{a^2}\frac{\Gamma(k-i)}{k^{k-i}}(\log k-\psi(k-i))$$

where $\psi(x)=d\log\Gamma(x)/dx=\Gamma'(x)/\Gamma(x)$. $\psi(x)$ can be expressed as a sum[12,13]

$$\psi(x)=-C+\sum_{s=0}^{\infty}\left(\frac{1}{s+1}-\frac{1}{x+s}\right) \tag{10}$$

where C is Euler's constant, but this summation is not in a form suited to numerical computation. A much more manageable form of (10) can be employed if x is an integer, say n, in which case (10) can be written

$$\psi(n)=-C+\sum_{i=1}^{n-1}\frac{1}{i}\cdot \tag{10a}$$

This summation can be evaluated approximately to a high degree of accuracy by the formula

$$\sum_{i=1}^{n-1}1/i\cong C+\log((n-1)+\tfrac{1}{2}). \tag{11}$$

We are using n in the neighborhood of 50 and for such values this approximation is good to one part in a hundred thousand. Now the right hand side of (11) is defined for non-integral values of n, and, in view of the regularity of (10), one can use (11) as an interpolation formula for finding $\psi(x)$ when x is not an integer, giving

$$\psi(x)\cong\log(x-1+\tfrac{1}{2}) \tag{10b}$$

We now return to the J's and substitute (10b) in (9) which gives

$$J_{k-i}=\frac{1}{a^2}\frac{\Gamma(k-i)}{k^{k-i}}\log\left(\frac{k}{k-i-\frac{1}{2}}\right). \tag{12}$$

Substituting (12) in (7) the latter becomes

$$P_{02}=p_0'A_0A_2k^{k-3}\left\{\log\left(\frac{k}{k-1\frac{1}{2}}\right)-2\frac{k-3}{k-2}\log\left(\frac{k}{k-2\frac{1}{2}}\right)+\left(\frac{k-4}{k-2}\right)\log\left(\frac{k}{k-3\frac{1}{2}}\right)\right\} \tag{13}$$

and it is only necessary to substitute the numerical values of a and k in (13) to get P_{02}. The spectroscopically determined constants of HCl are [14,15]

$$\nu_0=2940.7\ \text{cm}^{-1}\qquad r_0=1.279\times10^{-8}\ \text{cm}$$

$$\nu_0x=\ 53.58\ \text{cm}^{-1}\qquad J_0=2.645\times10^{-40}\ \text{cm}^2\ \text{gm}$$

and these values when substituted in (5) give

$$a=1.777\times10^{-8}\ \text{cm}^{-1}\qquad k=54.885. \tag{14}$$

[12] Nielsen, Handbuch der Gammafunktion: B. G. Teubner, p. 15.
[13] Jahnke und Emde, Funktionentafeln: B. G. Teubner, p. 27.
[14] Birge, Report, p. 230.
[15] E. C. Kemble, Jour, Opt. Soc. Am. 12, 1 (1926).

P_{02} can now be calculated and is

$$P_{02}=7.16\times10^{-11}\ p_0' \tag{15}$$

Similarly the matrix component P_{01} for the fundamental band can be calculated giving

$$P_{01}=7.67\times10^{-10}\ p_0' \tag{16}$$

Now α the absorption coefficient, is connected to the P's by the equation

$$\alpha_{nm}=\text{const.}\times\bar{p}\times e^{-E''/kT}\nu_{nm}(P_{nm})^2 \tag{17}$$

where $\bar{p}$ is the average of the statistical weights of the initial and final states; E'' is the energy of the initial state, and ν_{nm} is the frequency associated with the transition. If we compare corresponding lines in two bands, the ratio of their α's is given by

$$\left(\frac{\alpha_{02}}{\alpha_{01}}\right)_{calc.}=\frac{\nu_{02}}{\nu_{01}}\left(\frac{P_{02}}{P_{01}}\right)^2=1.983\times\left(\frac{.716}{7.67}\right)^2=0.0173. \tag{18}$$

The experimental value of this ratio is readily calculated. From Bourgin's[4] data the intensity of the third line in the negative branch of the fundamental band is 41.3×10^{-10} and from Table II the intensity of the same line in the harmonic band is 0.666×10^{-10}. So

$$\left(\frac{\alpha_{02}}{\alpha_{01}}\right)_{exp}=\frac{0.666}{41.3}=0.0161. \tag{19}$$

These two results differ by only 6 percent which is within the limits of experimental error.

The original justification for supposing that Morse's potential function (2) would fit the facts adequately for HCl was that the energy level formula given by Morse is of the right form. As far as vibrational energy levels are concerned, it is accurate, but when the information given by the rotational energy levels as to the shape of the potential function is taken into account, certain discrepancies are found. If we let $(r-r_0)/r_0=\xi$, then we can express U in the form

$$U(\xi)=K\xi^2(1+a\xi+b\xi^2+c\xi^3+\cdots),$$

and it is possible to compute K, a, b, and c from the rotational and vibrational energy levels. Kemble [15] has computed these constants for HCl on the basis of the Bohr theory, and Fues,[16] applying second order perturbation theory to an harmonic oscillator, has shown that at least K, a and b are the same as those given by the Bohr theory. Consequently Kemble's evaluation of these constants can be taken over into the wave mechanics.

To compare Morse's potential function with that given above, it is only necessary to expand (2) in powers of ξ about $\xi=0$ and compare coefficients. The numerical values of the coefficients obtained in these two fashions are:

[15] E. Fues, Ann. d. Physik 80, 396 (1926).

	Morse	Kemble
a	−2.27	−2.421
b	3.00	3.905
c	−2.93	−2.86

The constants a and b as obtained from the two analyses are seen to be materially different, and it is an interesting question, therefore, how accurate the intensity calculation based on Morse's wave functions would be. It is not possible to distinguish between the intensities given by Morse's method and the values determined experimentally, because the former do not fall outside the limits of accuracy of the measurements, so an attempt was made to see if a calculation of the intensities considering the molecule as a perturbed harmonic oscillator would give different results. The third and fourth power terms in ξ were introduced as perturbing terms and a second order perturbation carried out on the wave functions. The intensity calculated in this fashion was 60 percent higher than the experimental value, and it appeared that it would be necessary to carry out a third order perturbation to obtain precise results as the process does not converge rapidly.

The relative intensities of the lines in a band are more easily calculated, to a first approximation, as the contribution to each from the vibration is the same and hence cancels in considering only relative values. The two most important factors which vary from line to line are the Boltzmann factor and the statistical weight. Kemble[6] has shown that the average of the statistical weights for the initial and final states should be used and arrives at the formula $\alpha = \text{Const} \times \tilde{p} e^{-E''/kT} f(\nu)$ where $f(\nu)$ is a small correction term depending on the frequency and is due, largely, to the effect of centrifugal force on the oscillator. This function has been worked out by Kemble for the harmonic band, but, as his work has not been published, I shall give the analysis here.

We go back to Eq. (3), retaining, this time, the term in j, j being the rotational quantum number and R the vibrational wave function obtained from the entire wave function Ψ, by the relation $\Psi(r\theta\phi) = (R(r)/r)\, Y(\theta\phi)$. The individual wave functions have two subscripts, one referring to the particular characteristic value which E (in Eq. (3)) takes on and the other to j. We shall assume that Eq. (3) with the term in j left out has been solved and wave functions R_{n0} obtained, though it will not be necessary to give these functions explicitly. The effect of the term in j upon these functions can then be determined by considering it as a perturbation.

According to the ordinary procedure in perturbation problems[17] we start from the fact that Eq. (3) is of the type

$$L(R) - \lambda M_j(r) R + \beta E R = 0 \tag{20}$$

where $L(R)$ is a self-adjoint differential expression; $\lambda M_j = j(j+1)/\beta r^2$ and $\beta = 8\pi^2\mu/h^2$. The wave functions and energy levels are expanded in a series in λ

[17] A. Sommerfeld, Wellenmechanischer Ergänzungsband p. 170 ff.

$$R_{kj}=R_{k0}+\lambda u_{kj} \qquad (21)$$
$$E_{kj}=E_{k0}+\lambda \epsilon_{kj}$$

u_{kj} can be given by

$$u_{kj}=\sum_{i=0}^{\infty} j\gamma_{ki}R_{i0},$$

where

$$j\gamma_{ki}=\frac{jC_{ki}}{E_k-E_i}=\frac{1}{E_k-E_i}\int M_j R_{i0} R_{k0}\,dr,$$

so that

$$R_{nj}=R_{n0}+\sum_i{}' \frac{R_{i0}}{E_n-E_i}\int \frac{j(j+1)}{\alpha r^2}R_{n0}R_{i0}\,dr, \qquad (22)$$

where $\sum_i'$ means that in summation the term for which $i=n$ shall be left out. We are, of course, interested in the matrix component of the electric moment $p(r)$ given by

$$P_{n'j'n''j''}=\int p(r)R_{n'j'}R_{n''j''}dr \qquad (23)$$

Introducing the abbreviation

$$S_{ni}=\frac{1}{\beta}\int \frac{R_{n0}R_{i0}}{r^2}dr,$$

and substituting (22), (23) can be written

$$P_{n'j'n''j''}=\int p(r)R_{n'0}R_{n''0}\,dr$$
$$+\int p(r)\left\{R_{n'0}j''(j''+1)\sum_l{}'\frac{S_{n''l}R_{l0}}{E_{n''}-E_l}+R_{n''0}j'(j'+1)\sum_l{}'\frac{S_{n'l}R_{l0}}{E_{n'}-E_l}\right\} \qquad (24)$$

The last step assumes that in Eq. (22) the terms in S are small compared with those in R_{n0} and that consequently in (24) the products of two terms in S will be negligible, this assumption being justified by the fact that the rotational distortion of intensities is small.

If we define I by

$$I_{n'n''}=\int p(r)R_{n'0}R_{n''0}\,dr, \qquad (25)$$

it is easily verified that, owing to the orthogonality of the R_{n0}'s, and the fact that they are normalized, $I_{nn}=p_0$ and $I_{n0}=p_0'\int rR_{n0}R_{m0}\,dr$. That is to say, the I's are simply the matrix components of the transitions for the unperturbed anharmonic oscillator. Again, since $(r-r_0)/r_0$ is small compared to 1 whenever Ψ is appreciable, $1/r^2$ can be expanded in a series about r_0 and the expressions for S simplified, the result being

$$S_{nm}=-\frac{2}{\beta r_0^3}\frac{I_{nm}}{p_0'} \quad \text{if} \quad n=m$$
$$=-\frac{1}{\beta r_0^2} \quad \text{if} \quad n=m \qquad (26)$$

Substituting these expressions for S and I in (24) gives

$$P_{n'j'n''j''}=I_{n'n''}-\frac{2}{\beta r_0^2 p_0'}\sum_l{}'''I_{n'l}I_{n''l}\left\{\frac{j'(j'+1)}{E_{n'}-E_l}+\frac{j''(j''+1)}{E_{n''}-E_l}\right\}. \quad (27)$$

In substituting the values for the harmonic band where $n'=2$ and $n''=0$, we know experimentally that $I_{03}\ll I_{00}$ and it is evident that $I_{00}\cong I_{11}\cong I_{22}$, so we need consider only 3 terms in (27) (i.e. $l=0$, 1 and 2) and, if we substitute $E_n-E_m=h\nu_0(n-m)$ and carry out the summation over three terms, we get

$$P_{2j'0j''}=I_{20}-\frac{2}{\beta r_0^2 p_0'}\left[\frac{I_{20}I_{00}}{2h\nu_0}j'(j'+1)+\frac{I_{21}I_{01}}{h\nu_0}\{j'(j'+1)-j''(j''+1)\}-\frac{I_{22}I_{02}}{2h\nu_0}j''(j''+1)\right] \quad (28)$$

Now $1/h\beta r_0^2=B_0$ and $B_0(j'(j'+1)-j''(j''+1))=\nu-\nu_c$ where ν_c is the frequency of the center of the band, and if we substitute this relation, together with the value of I_{00}, into Eq. (28) we have

$$P_{2j'0j''}=I_{20}\left[1-\frac{2(\nu-\nu_c)}{r_0p_0'\nu_0}\left\{\frac{p_0}{2}+\frac{I_{21}I_{01}}{I_{02}}\right\}\right]. \quad (29)$$

The second term in the square bracket is small compared to the first so that, in taking ratios of the P's we can expand in series and omit second order terms. If we let

$$a=\frac{2}{r_0p_0'\nu_0}\left\{\frac{p_0}{2}+\frac{I_{01}^2}{I_{02}}\right\},$$

then $P_{2j'0j''}=I_{02}[1-a\Delta\nu]$. By Eq. (17) we have the relation

$$\frac{\alpha_{02m}}{\alpha_{023}}=\frac{\nu_m}{\nu_3}\frac{I_{02}^2}{I_{02}^2}\frac{[1-a\Delta\nu_m]}{[1-a\Delta\nu_3]}\frac{\bar{p}_m}{\bar{p}_3}e^{-(E_m''-E_3'')/kT}=\frac{\nu_m}{\nu_3}\{1+2a(\Delta\nu_3-\Delta\nu_m)\}\frac{\bar{p}_m}{\bar{p}_3}e^{-(E_m''-E_3'')/kT} \quad (30)$$

Taking the values of ν and ν_c fr[illegible]mes' work,[2] that of p_0 from Bourgin's paper and using the empirical values of I_{01} and I_{02} as found, respectively, in Bourgin's paper and in this one, $\alpha_{02m}/\alpha_{023}$ was calculated for the first nine lines of the negative branch and the values so obtained are tabulated in Table II column 6 and a graph of the values of the ratio of the calculated to observed values of the α's is given in Fig. 5. The difference between observed and calculated values is never over 4 percent and the extreme range of the points is only 5 percent. The mean of the ratio's of the calculated to experimental values is within 1.5 percent of being 1.

In Table II the values of b, the half-width of the lines, are given for the first five lines as calculated from Bourgin's second method. Owing to the steepness of the curves, this method does not give b with any precision, as

can easily be seen from the great spread of the values. The increase of the isotope doublet separation[9] is the obvious place to look for a cause of the increase in b with ordinal number. On the basis of Loomis' formula for isotope separation[18] one can readily calculate that in the first five lines of the negative branch of this band the change in separation of the doublet would be three or four percent of the total separation. The tabulated values of b are the widths of a symmetrical, somewhat arbitrarily shaped line which is made to

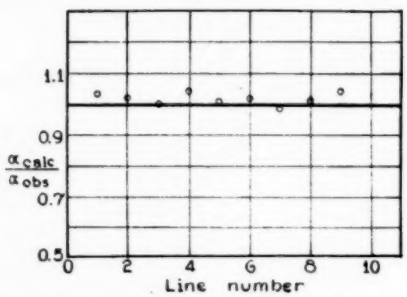

Fig. 5. Graph of the values of the calculated and observed values of the α's.

fit the actual doublet. If the small satellite line materially overlaps the larger one, it is possible that the value of b would be extremely sensitive to the doublet separation. Without going into a quantitative treatment of this broadening which would, at best, be extremely cumbersome, one can say that the observed increase of b with line number seems plausible.

The author wishes to acknowledge his indebtedness to Professor E. C. Kemble who interested him in the subject and whose advice and suggestions have been indispensable in carrying out this research.

[18] F. W. Loomis, Report, p. 260 ff.

ON A RESONANCE-FLUORESCENCE PHENOMENON IN THE CYANOGEN SPECTRUM

By Harold T. Byck
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(Received June 10, 1929)

Abstract

In a study of the spectra of organic compounds excited by streaming active nitrogen, the intensification of certain pairs of lines in the violet CN bands was observed. This phenomenon was reported recently by Herzberg who likened this intensification to the resonance-fluorescence of iodine. The cause, according to Herzberg, is absorption of radiation of short wave-length from nitrogen bands in the far ultra-violet. Experiments were made to test this explanation. Radiation from the nitrogen discharge was found to have no effect on the appearance or non-appearance of these intensified doublets. Additional experiments were made to observe the effect of pressure on the appearance of the intensification, and it was found that such intensification depends upon the pressure under which the excitation of the CN spectrum occurs. It appears that the intensification results through collision with some higher-energy atomic or molecular species whose formation is suppressed at higher pressures.

HERZBERG,[1] in several recent papers reporting a spectrographic study of the nitrogen after-glow, makes note of a peculiar phenomenon in the cyanogen bands developed in the after-glow. His photographs show groups of pairs of lines which, on comparison with the violet cyanogen bands developed in the carbon arc burning in air, seem to coincide with certain lines of these bands. The bands are of such low intensity relative to these particular lines that the photographs show these abnormally intense lines but few if any of the other lines making up the bands.

In a study of the spectra of organic compounds excited by streaming active nitrogen, to be reported shortly, the writer noticed this same phenomenon in the λ4606(0,2), λ4216(0,1), and λ3883(0,0) bands of the violet cyanogen system. The intensified doublets appeared in these band-groups with all the compounds used in the study, the only difference being slight variations in intensity from compound to compound, due perhaps to the variation in pressure necessary to draw a sufficient amount of the compound into the stream of active nitrogen. With all the compounds used, the violet cyanogen system is well developed, and even in active nitrogen alone, traces of carbon compounds from stopcocks are sufficient for the development of these bands. The intensity distribution within the bands is that characteristic of bands developed at low temperatures such as exist in the active nitrogen. The lower quantum rotation-levels are favored and the structure of the band at its origin is plainly discernible. In the λ4216 CN band, the position of the missing line is clearly defined, and the rotation lines are plainly resolved, to $m = 14$

[1] Herzberg, Naturwissenschaften **8**, June, (1928) 464; Ann. d. Physik **86**, 189 (1928); Zeits. f. Physik **49**, 512 (1928); Zeits. f. Physik **52**, 815 (1929).

in the P branch, which has the head, and to $m=22$ in the R branch. This is in marked contrast to the appearance of the same bands in the carbon arc,[2] where the higher quantum levels are favored and the structure of the origin is obscured by the P branch lines corresponding to transitions between these higher levels.

Chloroform introduced into active nitrogen gives these bands especially strong. This spectrum was photographed first with a Hilger $E1$ quartz spectrograph and the intensification was so marked as to permit the use of higher dispersion. The glass train was substituted in the spectrograph, giving a dispersion of 4.5A at λ4200, and the λ4216 group was photographed. The accompanying enlargement (Fig. 2) shows this group to good advantage, the dots marking the intensified lines of the first band (0,1). The intensified lines correspond, as pointed out by Herzberg, to the initial rotational states m 4, 7, and 15. These levels give the lines $R(3)$, $R(6)$, $R(14)$, and $P(5)$, $P(8)$, and $P(16)$. The writer's plates indicate still another initial state $m=13$ giving the lines $R(12)$ and $P(14)$.

The objection that this additional initial state gives these intensified P and R lines only because there is an overlapping of lines from other bands can be met by considering several of the intensified lines. The $R(12)$ line is nearly coincident with the head of the (1, 2) band in this sequence, but this band is weakly developed in active nitrogen and would contribute little to the observed intensity of this line. The $R(14)$ line appears to be multiple, and an examimation of Jevons' measurements[2] shows that two P branch lines of the (1, 2) band lie 0.7 and 2.35 wave-numbers to either side of this intensified line. The P branch lines $P(14)$ and $P(16)$ companions to the intensified $R(12)$ and $R(14)$ lines are observed to be intensified however and are free from close-lying lines, whereas $R(13)$ which coincides exactly with a line in the (1, 2) band shows no intensification. This indicates that the intensification is due not simply to the overlapping of lines.

Herzberg states that such intensification of certain lines in the cyanogen bands is probably due to absorption of radiation of very short wave-length from nitrogen bands in the far uitra-violet— a resonance-fluorescence phenomenon similar to that in iodine. The intensification is present in all the writer's photographs, and several experiments were made to test Herzberg's explanation.

The earlier pictures were made using an apparatus similar to that of Mulliken[3] for producing the stream of active nitrogen. A modified apparatus shown in Fig. 1 was next constructed in which radiation, other than the after-glow, was isolated from the point of contact of the active nitrogen with the organic vapor. A number of right-angle T bends, painted black outside, were interposed between the discharge tube and this point of contact. The discharge tube itself was covered with asbestos. A second discharge tube, which could be independently operated, was attached, directly, without a window or other obstruction, to the after-glow tube at this same point of contact.

[2] Jevons, Proc. Roy. Soc. **112A,** 407 (1926).
[3] Mulliken, Phys. Rev. **26,** 1 (1925).

In the one case, no radiation from any nitrogen discharge reached this point, while with the second tube operating in addition, such radiation must have been intensely concentrated at the CN emission area.

With acetylene in active nitrogen[4] duplicate exposures were made, first with the isolated discharge, then with both the isolated and the juxtaposed

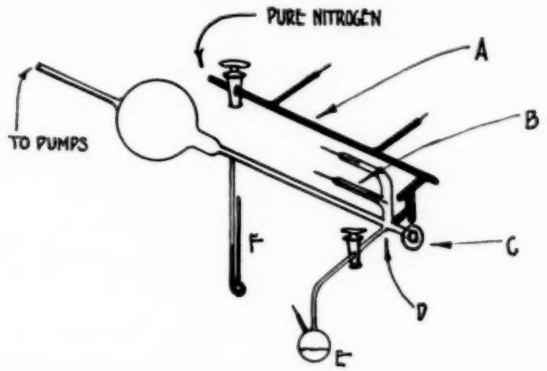

Fig. 1. Experimental arrangement: *A*, isolated discharge tube; *B*, secondary discharge tube; *C*, quartz window; *D*, point of contact—active nitrogen and organic vapor; *E*, reservoir with organic compound; *F*, manometer.

discharge tubes operating. If the intensification results from the absorption of radiation from the discharge, the first picture should show little or no effect, while the second picture should show a more marked effect. Actually

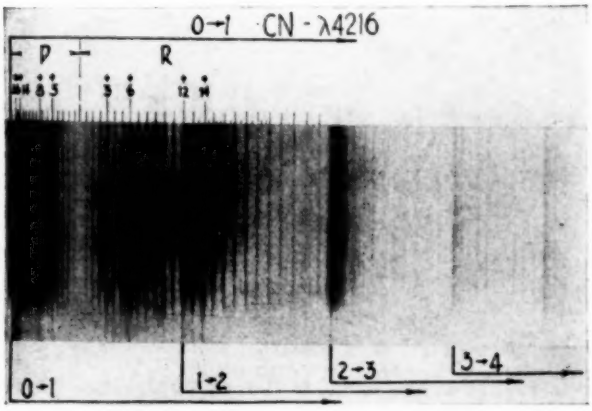

Fig. 2. Spectrum with chloroform in active nitrogen.

the doublets appear with about equal intensity in both. This seems to disprove Herzberg's statement of the mechanism of such intensification.

Next a series of such duplicate pictures was made in which the total nitrogen pressure in the system was varied for each pair of exposures. In the pictures taken with 5 mm, 8 mm and 10 mm pressure, the doublets appeared

[4] In the work of Jenkins,[5] Jevons[2] and others, this doublet intensification did not occur when acetylene was used.

in both exposures, e.i. with single and double discharges. At 20–40 mm pressure the doublets were absent from both exposures. Thus there is some relation between the pressure under which excitation takes place, and the appearance or non-appearance of the intensified lines, but there is no influence due to radiation. This pressure relation would explain the non-appearance of the doublets in the work of Jevons,[2] Jenkins[5] and others, as well as the variation in intensity on some of the writer's plates.

The above experiments on the effect of radiation and pressure seem to indicate that the absorption of radiation, as suggested by Herzberg, is not the cause of this doublet intensification. The energy necessary to raise the cold CN molecules to those initial states, from which transitions give observed intensified doublets, probably is imparted through collision with certain high-energy molecular or atomic species. These higher-energy species are sensitive to pressure, their formation being suppressed at high pressures.

The writer wishes to express his appreciation and gratitude to Dr. R. S. Mulliken, under whom this work was carried out, for his advice and guidance.

[5] Jenkins, Phys. Rev. **31**, 539 (1928).

DISPERSION AND ABSORPTION LINE WIDTH IN THE ALKALI VAPORS

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(Received May 23, 1929)

Abstract

Measurements were made photographically at various vapor densities of the widths in absorption of the sodium *D* lines, and of rubidium 4201 and 4215. Stewart's line width equation was again verified, indicating that scattering produces the opacity at the edges of absorption lines, at low vapor densities. This equation has not previously been directly tested for higher series members. Photographic measurements of the refractivity of sodium vapor near the *D* lines were made, and increased precision obtained over the visual measurements previously reported. The dispersion is found to conform to the classical curve, within an experimental error of 1 percent. The form of the dispersion to line width relation is shown to remain unchanged for higher series members. A theoretical treatment of the line width equation is given, indicating the modifications which quantum theory introduces. The form of the equations remains unchanged, but the number of molecules active in scattering is made explicit. "Negative line width" is introduced, corresponding to the negative term in the dispersion formula, but the correction would be small except at high temperatures.

Line Width

TO MEASURE the widths of the absorption lines, the various alkali metals were distilled into Pyrex tubes under vacuum, and after sealing off, were put into a resistance furnace, 35 cm long, within which the temperature could be controlled accurately. Using a 1000 watt tungsten lamp for a source, the lines were photographed in absorption by the aid of a grating spectrograph, showing 6 angstroms to the mm. The lines were photographed at various temperatures, and measured on a microscope.

Figure 1 shows the results, the logarithm of line widths being plotted against the log of vapor density. The crosses represent the *D* lines of sodium, and the circles 4201 and 4215 rubidium. Using the vapor pressures of Rowe,[1] the observed temperatures were translated into vapor pressures, and dividing by the Loschmidt number, into vapor densities. Each point represents the average of three measurements of one spectrogram of the absorption line at a known temperature. Each line was photographed twice at each temperature. The range of temperatures covered was from 200° to 380°C. Two tubes of rubidium were used, giving practically identical results.

Errors in the assumed vapor density due to time lag after the temperature of the furnace was changed were shown to be within the errors of measurement, by photographing the same line at various intervals after the furnace had reached a given temperature. Errors due to small variations in the photo-

[1] Rowe, Phil. Mag. **3**, 538 (1927).

graphic exposure were also found to be negligible, though they are considerable if the exposures are much altered. Thus on a black background, lines are measured less wide than on a lighter background. In this case, doubling the exposure time gave about 7 percent lower values. The time of exposure was therefore kept constant.

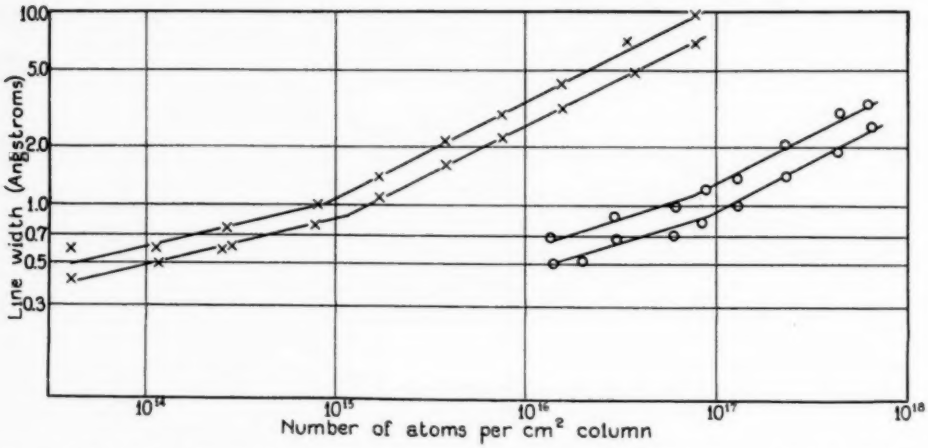

Fig. 1. Variation of line width with number of atoms in line of sight. Crosses are Na D lines, circles are Rb 4201 and 4215.

Stewart's equation[2] for line width is:

$$w=(6\pi)^{1/2}a\lambda_0(N/k)^{1/2} \tag{1}$$

where w is the width of the line, as measured between two points of minimum observable contrast, a is the "electromagnetic radius of the electron" ($2/3\ e^2/mc^2$, or 1.88×10^{-13} cm), N is the number of *active* atoms in unit column in the line of sight, and k is the contrast factor, i.e., the contrast at the observed "edge" of the line, such that the intensity ratio here is $1/(1+k)$ to the continouus background.

The formula assumes that scattering is the cause of the opacity at the edge of the line, at low vapor density. It was verified to order of magnitude by Fairley[3] for the sodium D lines. It is in this work shown to hold to 5 percent, the experimental error, for both resonance and higher series lines.

The equation calls for variation of the line width proportional to the square root of the number of atoms in the line of sight. The curves justify this relation for widths above the "resolving power break"[4] at one angstrom. Below this point the lines are measured too wide, due to the insufficient resolving power of the instrument. The slope of the straight line relation for sodium in Fig. 1 shows that the width varies as the 0.49 ± 0.02 power of N; and as the 0.47 ± 0.05 power for rubidium. The displacement along the axis of N between the straight lines for D_1 and D_2 shows that the ratio of

[2] J. Q. Stewart, Astrophys. J. **59**, 30 (1926).
[3] Fairley, Astrophys. J. **67**, 114 (1928).
[4] Korff, Phys. Rev. **33**, 584 (1929).

the number of atoms active in producing D_2 to those active in D_1 is $(1.8 \pm 0.2):1$, as compared to the accepted[5] value of 2:1. For Rb the value is thus found to be $(2\pm 0.2):1$.

Now solve Eq. (1) for k, taking the observed width of D_2 as 1 angstrom, when the vapor density was 6×10^{13} atoms per cc. As the tube was 23 cm long, the number of atoms in unit column was 138×10^{13}. But as only 2/3 of the sodium atoms are supposed to be active in producing D_2, (see Eq. (7), below) the effective N is 9.2×10^{14}. Taking (a) as 1.88×10^{-13}, we get $k=0.21$. This agrees well with the value of k obtained in previous work,[4] especially considering possible errors in the best vapor pressure determinations. The former value was obtained independent of vapor density. An independent study of the value of k is being undertaken. Similarly for Rb 4201 a width of 1 A. U. was observed at 6×10^{16} atoms per sq. cm column. Assuming k as 0.02, and substituting in Eq. (7) below, neglecting the "negative" term, f_{kj} is found to be 0.028. This work thus shows that 2.8 percent of the Rb atoms are "active" in 4201, and 1.4 percent in 4215. The values are uncertain, however, due to uncertainties in k and vapor pressure.

The rubidium lines were observed at vapor densities greater than 5×10^{16} atoms per cc to broaden unsymmetrically, i.e., to fuzz to the red, as Fuchtbauer[6] observed.

Potassium 4044 and 4047 were also observed but due to experimental difficulties were not observed above the "resolving power break." Up to this point, however, the lines behaved as did rubidium.

The rubidium lines 4201 and 4215 are second members of the series $(1S–3P)$ Equation 1 had not been previously tested for other than resonance lines. It is of considerable astrophysical interest, as it assists in quantitative analysis of stellar atmospheres.

Refractive Index

Photographic measurements[7] were made of the refractive index of sodium vapor near the D lines, employing the interferometer-spectroscope method previously described.[8] The method differs from the gas-interferometer method of Puccianti.[9] By measuring the plates on a microscope the positions of the fringes and the line width could be simultaneously measured, and accuracy over the previously described[4] visual observations was increased. Figure 2 shows the results, the refractive index (in phase shifts) being the ordinate, and wave-length the abscissa. The refractive index conforms to the classical equations (2 and 3, below) to within 1 percent, the limit of accuracy of the observations; more precisely, $\zeta\beta$ was observed equal to a constant (Eq.(4)) to this accuracy. In Fig. 2, the line width was 1.9 angstroms. For different line widths, families of such curves are obtained.

[5] Minkowsky, Zeits. f. Physik **36,** 839 (1926); Ladenburg, Zeits. f. Physik **4,** 469 (1921).

[6] Fuchtbauer, Phys. Zeits. **21,** 322 (1920).

[7] This paragraph was the substance of a paper presented at the April 18, 1929 Phys. Soc. meeting. (Abstract 20).

[8] Stewart and Korff, Phys. Rev. **32,** 676 (1928).

[9] Puccianti, Il Nuovo Cim. **2,** 257 (1901).

The work on line width has shown that higher series members also conform to Stewart's line width equation, and the work of Bevan[10] and Wood[11] and its discussion by Herzfeld and Wolf[12] has shown that the refractive index associated with these lines conforms to the Lorentz or Sellmier form (Eq. (2)). Thus the form of the relation between refractive index and line width (Eq. (3) or (4)) should remain unchanged for higher series members. It is planned to test it with the interferometer.

As in the case of the resonance line, the higher series members thus also behave as simple oscillators. The response of the atom to the incident radiation is according to the first spherical harmonic. For higher harmonics the effective form of the response would be different.[13]

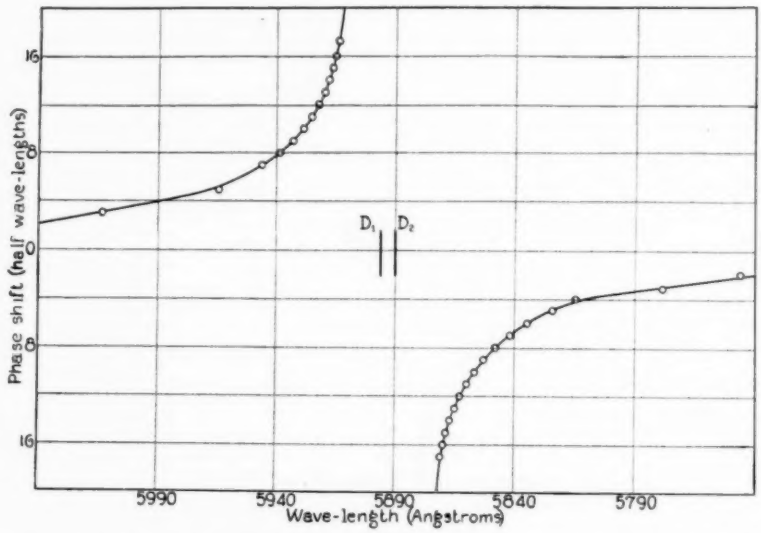

Fig. 2. Refractive index of sodium vapor. Observed points, theoretical curve (Eq. (1)).

The question arose as to whether the work of Schüler on hyperfine structure would in any way invalidate this conclusion concerning a simple oscillator. He has shown[14] that the sodium *D* lines and many other alkali lines have such a fine structure. The splitting up of the oscillator into components has been considered[4], however, in connection with the Zeeman effect, and shown not to affect appreciably the response of the atom, and thus the form of the line width or dispersion equations or the equation connecting them. (Eqs. (1) (2) and (3)).

Theoretical Discussion

The well-known Lorentz dispersion equation[15] is

[10] Bevan, Proc. Roy. Soc. **A83,** 421 (1909); **A84,** 209 (1910); **A85,** 54 (1911).

[11] [illegible] Phil. Mag. **8,** 293 (1904).

[12] Herzfeld and Wolf, Ann. d. Physik **76,** 71 (1925); **76,** 561 (1925).

[13] Lamb, Proc. Camb. Phil. Soc., Stokes. commem., 349 (1900); J. Q. Stewart, J. Opt. Soc. Am. **11,** 581 (1925).

[14] Schüler, Naturwiss. **25,** 512 (1928).

[15] Page, Introduction to Theor. Phys., p. 469.

$$\mu-1=\frac{1}{4\pi}\frac{e^2}{mc^2}\frac{\lambda_0^3}{\lambda-\lambda_0}N \tag{2}$$

where μ is the refractive index, e the electronic charge, m the electronic mass, λ_0 the wave-length of resonance, and N the number of atoms active in producing dispersion.

Solving this equation for N, and substituting in Eq. (1) we obtain an expression relating line width and refractive index, being independent of N, the number of active atoms. This expression is:

$$\mu-1=\frac{3}{32\pi}\frac{\lambda_0}{\lambda-\lambda_0}\frac{mc^2}{e^2}kw^2. \tag{3}$$

This is identical with:

$$\zeta\beta=kw^2/8\pi^2a\lambda_0 \tag{4}$$

by a few definitions. Equations (3) and (4) were derived in former work,[8] and tested[4] using the resonance D lines of sodium.

The old quantum theory does not give the form of the equations, but introduces factors determining the number of "active" atoms. Ladenburg[16] has shown that what we have called the number of active atoms is

$$N=N_jf_{kj}=N_jA_{kj}g_kmc^2/g_j8\pi^2e^2\nu_{kj}^2 \tag{5}$$

where N_j is the number of atoms in state j, A_{kj} is the Einstein transition probability, g_j and g_k are the respective statistical weights of the states, m the mass and e the charge of the electron, c the velocity of light, ν_{kj} the frequency associated with the k to j transition.

Kramers[17] introduced "negative dispersion". The Kramers-Ladenburg[18] dispersion equation is:

$$\mu-1=\frac{1}{4\pi}e^2\lambda^3N_jf_{kj}\frac{1-N_kg_j/N_jg_k}{mc^2(\lambda-\lambda_0)} \tag{6}$$

It is well known that this reduces to the Lorentz equation when N_k is small compared to N_j. It has been checked by Kopfermann[19] in excited neon, and by Carst[20] for the Balmer hydrogen lines.

Now if we assume that the same number of atoms that produce the dispersion associated with a given line, produce the line itself, by scattering, we may substitute the quantum N value in the line width equation (Eq. (1)) including also the negative term. We get:

$$w=(6\pi)^{1/2}a\lambda_0\left[N_jf_{kj}(1-N_kg_j/N_jg_k)/k\right]^{1/2} \tag{7}$$

This should be a generalization of the classical equation, applying to higher series members and especially to cases where there are many atoms

[16] Ladenburg, Zeits. f. Physik **4,** 452 (1921).
[17] Kramers, Nature **113,** 673 (1926); **114,** 310 (1926).
[18] Ladenburg, Zeits. f. Physik **48,** 15 (1928).
[19] Kopfermann, Zeits. f. Physik **48,** 26 (1928).
[20] Carst, Zeits. f. Physik **48,** 192 (1928).

in higher states. The negative term diminishes the line width, hence the suggestion is to follow Van Vleck's[21] treatment of the dispersion equation and call this the equation for "differential line width." The number of active atoms is in this case, however, under the square root sign, and hence the the analogy is not exact.

For the relation between dispersion and line width, we see at once that if we eliminate the "number of active atoms" between Eqs. (6) and (7) we get the identical Eq. (3) of classical theory. Thus Eq. (3) remains unmodified by the quantum factor, and we should accordingly expect it to hold for higher series members.

Quantum mechanics has as yet not treated the relation between refractive index and line width, since the line width problem has not yet been solved. Dispersion has been treated, however, by the Schrödinger theory and the method of perturbations[22] for the case far from the line, and Dirac[23] has given equations for the case of resonance.

At the temperatures used in the above experimental work the negative term was too small to be observable, since N_k was small compared to N_j. An attempt to observe it in excited helium was unsuccessful. It is suggested, however, that the negative term in line width might be easier to detect than that in dispersion, since line widths are generally easy to observe, and k could be determined with a densitometer.

I wish to express my sincere appreciation of the criticism and advice of Professor J. Q. Stewart in the preparation of this work.

[21] Van Vleck, Phys. Rev. **24,** 330 (1924).
[22] Herzfeld, Handbuch der Physik **20,** 577 (1928).
[23] Dirac, Proc. Roy. Soc. **A114,** 710 (1927).

THE EFFECT OF HYDROGEN ON THE THERMIONIC EMISSION FROM POTASSIUM

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Abstract

Effect of surface conditions on the current value at a given temperature.—Observing the current at a given temperature after successive cleansings of a potassium surface by distillation followed by contaminations of the surface by hydrogen it was concluded that the large ($>>10^{-14}$ amperes $\cdot$ cm^{-2} at 180°C) thermionic currents frequently observed from potassium are due to hydrogen contamination, confirming the results of Fredenhagen.

Saturation of currents.—With a uniform field in the present apparatus it was shown that it is possible to saturate the thermionic currents observed from potassium at 150°C to 185°C; failure to saturate in the case of previous observers being probably due to non-uniform field conditions. Furthermore, even at temperatures below 100°C no evidence was found for a more important factor in the prevention of saturation than the non-uniform field.

The thermionic work function.—The larger currents were found to obey an equation of the Richardson type over a limited temperature range (150°C–210°C). A value of ϕ of about 1.3 volts was characteristic of the potassium surface after hydrogen contamination of a certain type. This value is similar to that found by Richardson and Young in the same temperature range. It was concluded that this value of ϕ was due to a layer of KH on the surface of the potassium, and that the emission was probably chemical rather than thermionic in origin, being due to the decomposition of the KH. Values of ϕ of 0.26 volts were found at temperatures from 100°C to 110°C which are of the order of Richardson's and Young's values at those temperatures.

Effect of hydrogen on conductivity of thin potassium layer.—The conductivity of a thin layer of potassium on a Pyrex insulating tube was greatly decreased by exposure to hydrogen.

Introduction

PREVIOUS thermionic work on potassium has been done by Fredenhagen,[1] and Richardson and Young,[2] but the conditions were in all cases rather unsatisfactory in certain respects.

Fredenhagen was mainly concerned with trying to show that the current measured was due to the presence of a gas (which he thought to be hydrogen) in the potassium and that the current could be made to disappear by complete removal of the gas. He distilled the potassium in vacuo two or three times and then sealed off his apparatus from the pump (charcoal tube attached) and heated the potassium at successively higher temperatures (250°C to 375°C) for many hours. His gas pressures before the sealing off were probably

[1] Fredenhagen, Phys. Zeits. **12**, 398 (1911); Berichte Deut. Phys. Ges. **14**, 384 (1912); Berichte Deut. Phys. Ges. **16**, 201 (1914).

[2] Young, Proc. Roy. Soc. **104A**, 611 (1923), O. W. Richardson and Young, Proc. Roy. Soc. **107A**, 377 (1925).

somewhere between 10^{-3} and 10^{-6} mm Hg since he used a Gaede rotary pump in his earlier work and later a molecular pump. Although his vacuum conditions after sealing off were doubtful, still he found that his currents decreased considerably during the continued heating; on the other hand, cooling the charcoal with liquid air had a negligible effect on their magnitude.

Richardson and Young set out to measure the saturation current as a function of the temperature and thus to determine the thermionic constants A_1 and ϕ for potassium under good vacuum conditions, as well as the photoelectric ϕ. Although they used a mercury vapor pump and obtained pressures of about 10^{-6} mm Hg they did not distill their potassium, but merely melted sticks of it in a side tube and allowed it to run into the main apparatus through a U tube. This procedure seems hardly consistent with their later attempt to work under the "best possible vacuum conditions."

They concluded that the negative currents measured (the positive current was negligible) were due to electrons which were emitted "thermionically" and not by some type of chemical action. In general, by plotting $\log_{10}(i/T^{1/2})$ against $1/T$ for a set of current-temperature measurements they obtained a curved line over the range covered, i. e., 20°C to 250°C. Such a curve could be expressed empirically by the sum of two terms of the type $A_1T^{1/2}e^{-b/T}$ which had a pair of values of the constants A_1 and b corresponding to each nearly straight end of the curve. Certain irregular effects, such as discontinuities in the current-temperature curves and also the occasional occurrence of straight "log plots," were observed, but not explained. The two values of b they took to imply the existence of two work functions.

Their thermionic current-voltage curves showed no saturation up to several hundred volts, as was also the case with those obtained by Fredenhagen. On the other hand, their photoelectric currents saturated very readily. This difference in saturation characteristics between the thermionic and photoelectric currents they tried to explain by assuming that the thermionic work functions were active in minute localized "patches" only. For since these work functions were less than that found photoelectrically, these "patches" would then be positive with respect to the main or photoelectric surface, so that the current from them might be expected to be difficult to saturate. This assumption regarding the distribution of the work functions was borne out by the smallness of both values of the constant A_1 as compared to its normal value.

To summarize the results of these observers, Fredenhagen showed that the large currents first obtained from potassuim were probably due to the effect of a gas, although this conclusion was somewhat doubtful, since the pressure in his sealed-off apparatus was unknown. The gas responsible for the effect was thought to be hydrogen. However, he did not show that there was not a thermionic current which was characteristic of the potassium itself remaining after the removal of the gas.

Richardson and Young, due to their methods of introducing the potassium into their apparatus without distillation most probably dealt with "gas modifications" of the potassium surface, as they themselves concluded.

Under these conditions they found evidence for two work functions which they thought to be active in localized patches only.

It seemed worth while to attempt to determine the thermionic constants of gas-free potassium, by working at lower pressures than Fredenhagen could obtain and by outgassing the metal by repeated distillations, which Richardson and Young did not do. Under such conditions it was hoped that the irregular effects, such as those observed by Richardson and Young, would be eliminated, and more consistent results could be obtained.

As an improvement over the apparatus previously used, the present apparatus was built with a concentric guard ring surrounding the circular collecting disk above the potassium surface. It was hoped that by the use of a uniform accelerating field for the thermions, saturation could be obtained with a difference of potential less than the ionization potential of the potassium vapor (i.e. 4.3 volts). Thus saturation of the thermionic current would be obtained without introducing an error due to ionization by collision in the vapor. Such an error was always introduced by the high voltages used by the previous observers in the vain hope of obtaining saturation.

The intention was to cover the range of 250°C down to as low a temperature as possible. The complications introduced by the addition of the guard ring made it seem unlikely that the apparatus could be used above this upper temperature, due to the high vapor pressure of the potassium. The magnitude of the current to be expected from gas-free potassium could not be determined, since the proper value of ϕ to be used in extrapolating down from Fredenhagen's smallest current value of 6×10^{-10} amp. $\cdot$ cm^{-2} at 360°C was not known. However, considering Richardson's and Young's currents of 10^{-9} amp. $\cdot$ cm^{-2} at 200°C from gas-filled potassium, it was hoped that the present apparatus, with a current sensitivity of 10^{-14} amp. $\cdot$ cm^{-2} per millimeter deflection, would cover a fair range below 250°C for the gas-free potassium.

Actually, the current from the potassium introduced into this apparatus by successive distillations was found to be of the order of 10^{-14} amp. $\cdot$ cm^{-2} at about 250°C, above which temperature it was found impossible to work. Accordingly, a study was made of the effect of hydrogen on the magnitude of the current and also on the thermionic constants. In addition, the reason for the non-saturation of the currents obtained by all the earlier observers was investigated.

Apparatus and Method

The experimental tube is shown in Fig. 1. The container was Pyrex and the metal parts were nickel. The potassium pool was heated by immersion in an oil bath to the level shown. The collecting electrode or disk (connected to A) was the end of the tube T; G was the guard ring (connected to B); R_1 and R_2 were cylinders provided for cooling the disk and guard ring by radiation to a split metal water jacket fitting closely outside the tube. The cylinder C supported the lower electrodes by the Pyrex tubes P, and was

intended to remain at as low a temperature as possible. This was in order that the shielding tube *S* might protect the disk insulation from receiving a conducting film of potassium. The diaphragm *D* served a similar purpose between the pool and the supports of *C*. The tube was evacuated by a mercury vapor pump backed by an oil pump, with the usual liquid air trap between the tube and the pumps. A McLeod gauge was connected to the line between the vapor trap and mercury pump. In order to insure against the presence of contaminating vapors there were no wax or cement joints on the tube side of the liquid air trap. The hydrogen admitted to the tube was at first from an electrolytic generator connected to the oil pump lead, and later from a palladium tube sealed to this lead.

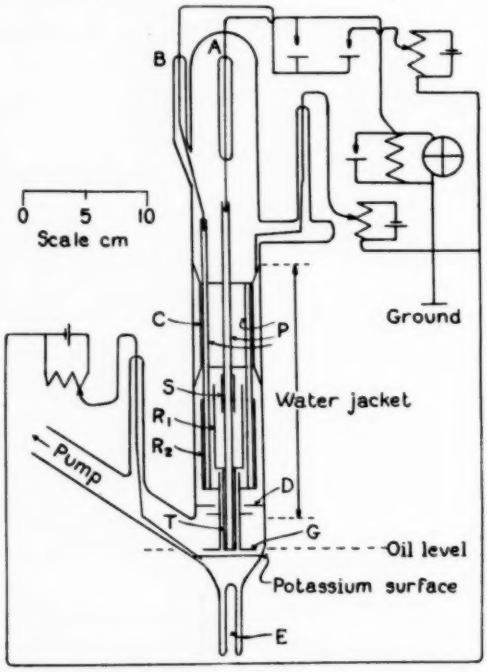

Fig. 1. Experimental tube.

The potassium in lumps, as taken from kerosene, was scraped and washed in carbon tetrachloride, melted through funnels into a capsule in a rough vacuum, distilled twice into bulbs which were sealed off successively (on a separate vacuum system similar to the above), and then distilled twice more into a reflex condenser connected to the slanting pump lead of the tube (Fig. 1). Here it was heated for several hours and finally distilled over and allowed to run down the pump lead into the tube. The distillation temperatures were about 450°C and the tube was also previously baked out at that temperature.

During the last distillation, and afterwards until hydrogen was admitted, the pressure was always less then 10^{-6} mm Hg since the mercury pump was run continuously. The runs taken after the hydrogen was admitted were

with the mercury pump in use, unless otherwise stated and the pressure was less then 10^{-6} mm Hg up to 200°C, perhaps rising to 10^{-5} mm Hg at 240°C. Between runs the pressure could be held as low as 10^{-5} mm Hg for several days by a mercury cut off. Liquid air was always kept on the trap.

The temperature of the potassium surface was measured by thermocouples placed in the re-entrant tube *E* and 1/4°C could be estimated on the scale of the millivoltmeter used with them.

The currents were measured by a Compton electrometer with a sensitivity of 2000 to 3000 mm per volt, using the constant deflection method, the shunt being a series of graphite resistances of which the largest was 4×10^{10} ohms, giving a maximum current sensitivity of 1.2 to 0.8×10^{-14} amp. per mm deflection. It was possible to measure separately currents from the potassium to the central disk (referred to as "*D*" currents) or to both it and the guard ring *C* (referred to as "combination" or "*C*" currents).

An interesting effect of hydrogen upon the resistance of the insulation of the disk was observed, since the shielding was not adequate, and enough potassium condensed on the former to render it slightly conducting. On admitting hydrogen to a few mm Hg pressure, the insulation resistance would increase by a factor of 10^3 or 10^4 in a few minutes (from say 10^9 to 10^{12} or 10^{13} ohms). Furthermore, this hydrogen treatment of the insulation formed a protecting layer which withstood the presence of more vapor without becoming conducting.

One of the greatest difficulties encountered in working with this apparatus was the fact that the guard ring *G* and disk became hot enough to emit electrons, since their coating of potassium rendered them very active thermionically. This made it necessary to heat and cool the potassium rather rapidly so that these electrodes would not have time to reach temperatures high enough for such emission to become troublesome. The rate of heating used was such that the potassium temperature rose from 140°C to 240°C in 50 minutes and on cooling fell from the latter value to the former in 115 minutes.

Even with these fairly fast rates, at the higher temperaures and while cooling, the negative current to the disk from the guard ring, was sometimes troublesome even with the latter at zero potential, but the current of the opposite sign (i.e, when the guard ring was made positive) was negligible.

Hence, during a run, to prevent the guard ring from contributing to the negative current measured from the potassium to the disk, the former was put at a potential of +1.0 volt. This drew some electrons to *G* that would have reached the disk if *G* had been at zero potential, but it was possible to allow for these. To make sure of the absence of other spurious currents, and disturbing effects, such as varying zero shifts due to voltaic action across the slightly conducting film on the disk insulation below the can *C*, direct insulation leaks, electrons leaving the disk, or positive ion emission from the guard ring, deflections were read for pool potentials of −3, +2, +7 volts, for each current value measured to the disk. (Can *C* always at zero potential. From the behavior of these readings, it seemed reasonably certain that the currents obtained were true saturation values of the therm-electron current

from the potassium surface, the positive current from the potassium being less than 1 percent of the negative. The fact that the currents were saturated at -3 volts on the pool will be shown later by detailed current-voltage curves. Photoelectric currents were always found to be absent at low temperatures before the thermionic currents were measureable. (Light proof cover used to enclose tube.) When currents were measured to the "combination," readings were taken in a similar manner to the above. These currents did not, however, saturate, as will be shown below.

In making plots of the currents to determine the thermionic constants the term $\frac{1}{2}\log_{10}T$ varied so slightly in the range covered that its subtraction from $\log_{10}i$ before plotting against $1/T$ only caused a change in slope of about 1 percent. Hence simply $\log_{10}i$ was plotted against $1/T$, which amounts to assuming the equation

$$i = A_1 e^{-b/T} \tag{1}$$

The work function, $\phi = (bk/e) \times 10^{-8}$ volts, (k = Boltzmann constant) was computed from these plots, The constant A_1 (electrons per cm^2 per degree$^{1/2}$ per second) was computed from the plots taking account of the term $\frac{1}{2}\log_{10}T$ for the sake of comparison with Richardson's and Young's values.

Results

1. *The effect of the potassium surface-conditions on the "D" currents at a given temperature.* The D currents at a temperature of 180°C are found to exhibit the following behavior with changes in the surface conditions of the potassium:

(a) The currents obtained from freshly distilled surfaces* when heated in a "good" vacuum were of the order of 10^{-14} amps. per cm^2.

(b) The current obtained from an initially fresh surface exposed to a relatively low pressure of hydrogen (4×10^{-2} mm Hg), during the heating, was not appreciably greater than the currents from the "fresh" surfaces heated in a "good" vacuum.

(c) The current obtained from a surface first exposed to hydrogen at a relatively high pressure (4 mm Hg) and low temperature (20°C) for an appreciable time (2 hr) and then heated in a "good" vacuum was but very little greater (factor of 5) than the "fresh" surface currents.

(d) On the other hand, the currents obtained from surfaces first exposed to hydrogen at similar pressures (3–5 mm and also 20 mm) but at a much higher temperature (150°C) for similar lengths of time (2–4 hrs) and then heated in a "good" vacuum, were from 50–100 times greater than the "fresh" surface currents.

These results are in accord with those of Fredenhagen (see Table I, 11 and 12,) since they both show, by inverse processes, that the large currents

* This was the case whether the "fresh" surface was produced by the initial distillation of the potassium into the apparatus, or by distilling down condensed potassium from the top of the apparatus. This treatment was necessary after 5–6 runs to remove conducting layers of potassium from the insulation, and formed a layer of the metal 2–3 mm thick on top of the pool.

to be obtained from a potassium surface are due to the effect of a gas. The gas was thought by Fredenhagen to be hydrogen, as was here evidently the case.

TABLE I. Notation: *E* following a current value means that it was obtained by extrapolation from the value at the temperature in parenthesis, assuming Eq. (1) and using the average *D* value of ϕ (1.28 volts). This average *D* value of ϕ was obtained from 9 heatings and 7 coolings whose values of ϕ ranged from 0.97 to 1.43 volts. "Bake" refers to baking the top of the tube free of short circuiting layers of potassium. Current values of previous observers are for 4–5 volts accelerating potential, except number 14, which is for 235 volts.

Experimental Conditions	Number	Current at 180°C (amp $\times 10^{-14} \cdot cm^{-2}$ receiver)		ϕ volts		A_1 (electrons $\cdot cm^{-2} T^{-1/2} sec^{-1}$)	
		D	*C*	*D*	*C*	*D*	*C*
Observer-Author.							
Pot. just dist. into tube	1	1.0-E (2.5–190°C)					
First heat after bake	2	0.15-E (7.5–240°C)					
Heating (to 248°C after "H_1 heat")	3	46		1.21		4.2×10^{18}	
Cooling (to 155°)	4	3		1.15		7.1×10^{16}	
Next heating (to 243°C)	5	12		1.14		1.7×10^{17}	
Cooling (to 107°C)	6	3	see Fig. 4	1.37		1.2×10^{19}	
Next heating (to 238°C)	7	17		1.18		6.6×10^{17}	
Cooling	8	3		1.25		7.3×10^{17}	
Heating (to 248°C after "H_2 heat")	9	30	660	1.17	1.21	1.1×10^{18}	7.0×10^{19}
Cooling	10	see Fig. 5.			1.78		5.9×10^{64}
Average Value				1.28			
Observer—Fredenhagen.							
After 2 hours heating	11	650-E (279°C)					
After 56 hours heating	12	6.5-E (351°C)					
Observer—Richardson and Young.							
After several heatings	13	37,000					
Pot. just introduced	14	9					

Furthermore, an exposure to hydrogen at relatively high pressures and temperatures for an appreciable time was needed to bring about the large increase in current. Accordingly, it seems very likely that this increase in current was not due to hydrogen physically absorbed in the potassium surface, but rather to the formation of a layer of hydride on the surface.

2. *The current-voltage curves at a constant temperature.* Due to the high vapor pressure of the potassium, it was only found practicable to maintain the constant temperature conditions necessary for taking current-voltage curves at temperatures from 150°C to 185°C. Even at these temperatures it was necessary to have hydrogen present in the apparatus at a pressure of 3 to 4×10^{-2} mm Hg. This cut down greatly the diffusion of the potassium vapor (its pressure is 10^{-3} mm Hg at 162°C)[3] and thus preserved the insulation.

Accordingly all the curves in Figs. 2 and 3 were taken with the above pressure of hydrogen present, except the 85°C curve in Fig. 3, for which the pressure was less then 10^{-6} mmHg. The curves in Fig. 2 (scales adjusted) were for "*D*" currents at 151°C and 182°C with the guard ring at zero potential, but similar curves were obtained when it was +1.0 volt. They show saturation at 2 volts, followed by a slight rise between 4 and 5 volts due to impact ionization of the potassium vapor. Hence it is probably correct to assume that saturation would be obtained at a potential of 3 volts, even at the higher temperatures.

In regard to the reason for the non-saturation of the thermionic currents observed by both Fredenhagen, and Richardson and Young, the above results suggest that it was due to the non-uniform fields in their apparatus, as was mentioned above. Field conditions similar to theirs existed in this

[3] International Critical Tables.

apparatus in the case of the "*C*" or "combination" currents. Such *C* current curves (scales adjusted) are shown in Fig. 3, and are seen to show incomplete saturation. Hence the non-uniform field is seen to be a sufficient reason for not obtaining saturation at a few volts potential at temperatures of 150°C to 185°C under the general conditions of this type of experiment.

Now Richardson and Young found even poorer saturation at temperatures below 100°C than at 150°C to 200°C. Since the *D* current was below the limit of this apparatus at about 150°C, the only evidence obtained concerning such a type of behavior was as follows. Comparing the 85°C *C* current curve in Fig. 3 with the *C* current curves in the higher temperature range, it is seen to be almost indentical with them in form. Hence there is no evidence that any more important factor than the non-uniform field enters in at lower temperatures to help prevent saturation. So the presumption

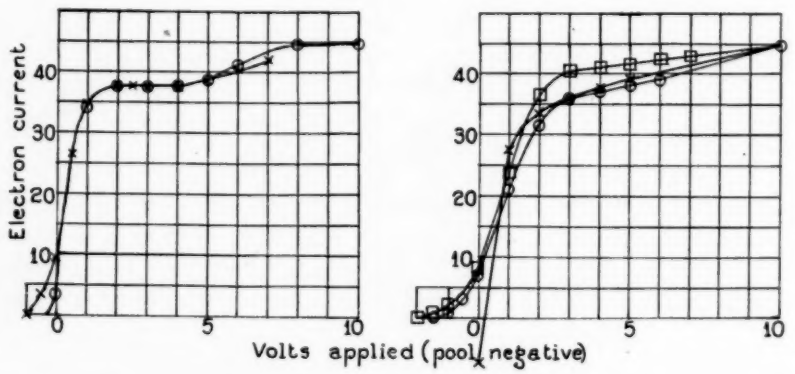

Fig. 2. "*D*" current-voltage curves. Circles: 151°C, 0.50×10^{-14} amp/div. Crosses: 182°C, 0.97×10^{-14} amp/div.

Fig. 3. "*D*" current-voltage curves. Squares: 160°C, 3.5×10^{-13} amp/div. Circles: 178°C, 1.4×10^{-12} amp/div. Crosses: 85°C, 1.3×10^{-14} amp/div.

is that the *D* currents would have been saturated at 85°C if they could have been measured.

3. *The temperature variation of the currents and the thermionic constants.* The temperature variation of the larger *D* currents (as produced by preliminary "hydrogen heating," see (d) under first part of results) and the *C* currents is most conveniently shown by the plots of $\log_{10} i$ against $1/T$. In Fig. 4 are shown the *D* currents for three successive heatings. It is seen that on both heating and cooling, the currents follow Eq. (1) over a fair portion of the range covered. These curves were typical for the larger *D* currents, though there was considerable variation in the temperatures at which the current broke away from the straight log plots on heating, and later decreased sharply.

This sudden decrease in current was apparently different from the similar effect observed by Richardson and Young, since on cooling their currents increased back to their values before the decrease and then fell with the temperature at values similar to those on heating. The sudden "decrease"

observed here is thought to be possibly due to a purification of the surface by drops of distilled potassium falling from above.

Considering next the C currents, in Fig. 5, curve 1 is a C current curve and curve 2 a D current curve taken during the same heating for comparison purposes. There is seen to be no sharp decrease of the C current similar to that shown by the D current, although on one run such a decrease was encountered at about 260°C. The C current is also seen to follow Eq. (1) over a fair range, although below about 110°C on heating and 200°C on cooling the curve bends upward. This curve is typical for the C currents.

From such log plots as these, values of ϕ and A_1 (taking account of the $T^{1/2}$ factor, as mentioned previously) were calculated and a few of these values

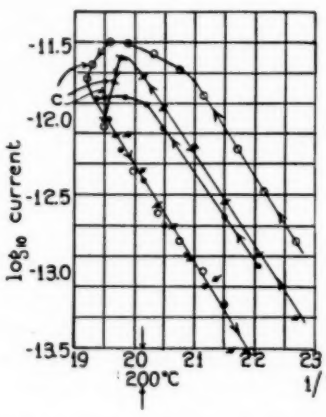

Fig. 4. "D" currents. Circles: init. temp. 20°C. Dots: init. temp. 155°C. Crossed dots: init. temp. 107°C. For values of ϕ see Table I, Nos. 3 to 8.

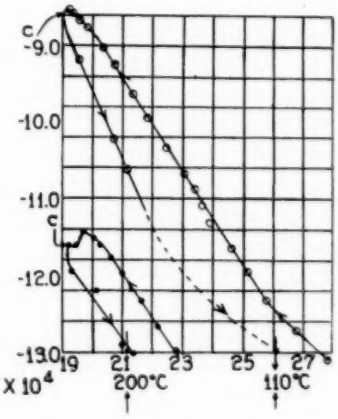

Fig. 5. Circles: curve 1, "C" current. Dots: curve 2, "D" current. For values of ϕ see Table I, Nos. 9 and 10.
Arrows designate direction of cycles. Heating current cut off at points "C."

are given in Table I. The effect of the superficial and other conditions on these constants may be summarized as follows:

Values of ϕ (a) For both the C and D currents under the surface conditions produced by the preliminary "hydrogen heating," the average value of ϕ was about 1.3 volts over the temperature range of 150°C to 210°C.

(b) For the C currents under the surface conditions for which the D currents were too small to determine a value of ϕ (i.e., when the effect of a "hydrogen heating" had been destroyed) the values of ϕ were much greater then 1.3 volts, varying from $1.64-2.24$ volts over the same temperature range.

(c) For the C currents at low temperatures (110°C to 100°C) the value of ϕ was 0.26 volts.

Hence it can be concluded that the "hydrogen heating" produces over the whole surface a modification of the potassium having a ϕ of 1.3 volts

in the higher temperature range. This value of ϕ agrees with those found by Richardson and Young (1.00 − 1.36 volts) in the same temperature range. Furthermore, the low temperature value of $\phi = 0.26$ volts agrees roughly with their corresponding value of 0.43 volts.

It is to be noted that although the surface condition produced by the "hydrogen heating" was the only one giving the low value of $\phi = 1.3$ volts for the C currents, nevertheless other surface conditions gave just as large C current values at 180°C as this surface condition did. This was not at all the case with the D current values. The discrepancy is probably due to the difference in physical conditions at the center and edge of the potassium pool.

Values of A_1. (a) For the C currents giving a value of ϕ of about 1.3 volts, the value of A_1 was of the order of 10^{21}. For the similar case of the D currents the values of A_1 were appreciably smaller, since the current densities of the D currents were about 1/5 to 1/20 of those of the C currents having the same value of ϕ.

(b) For the C currents giving values of ϕ from 1.64–2.24 volts, the values of A_1 ran as high as 10^{28}.

(c) For the C currents giving a value of ϕ of 0.26 volts, the value of A_1 was of the order of 10^{7}.

The values of A_1 of 10^{21} and 10^{7} are of the order of the values found by Richardson and Young under corresponding conditions.

The values of A_1 of the order of 10^{28} are 10^{3} times even the "normal" value of A_1 given by Richardson and Young as 3.8×10^{24} electrons per cm^2 per degree$^{1/2}$ per second. This "normal" value agrees with Dushman's value for tungsten[4].

Discussion

Considering the action of the "hydrogen heating" in producing a ϕ of 1.3 volts over the whole surface, it has been assumed probable that this process resulted in the formation of a layer of hydride on the potassium. The fact that such a formation of hydride is possible is substantiated by the work of Keyes[5] who found definite dissociation pressures for KH in the range of 200°C to 400°C. His value was 0.10 mm Hg of hydrogen at 215°C. Hence, the pressure used here during the "hydrogen heating" was sufficient to cause the formation of KH. The actual presence of the hydride was further confirmed by the observation of a ring of greyish-white scum at the extreme edge of the pool, drawn up there by surface tension, although the center of the surface was clean and bright. The appearance of this scum was similar to that of potassium and sodium hydrides as observed by Newmann[6], who found the hydrides to consist of white crystals which appeared greyish when dissolved in his K − Na alloy.

Accordingly it seems reasonable to conclude that the ϕ of 1.3 volts is due to the surface of the potassium being covered by a very thin layer of KH rather than to its being filled with hydrogen physically absorbed.

[4] S. Dushman, Phys. Rev. **25,** 338 (1925).
[5] Keyes, Jour. Am. Chem. Soc. **34,** 779 (1912).
[6] F. H. Newmann, Phil. Mag. **44,** 222 (1922).

On this basis, the fact that the current density for the *C* currents was larger than that for the *D* currents, although the ϕ's were both 1.3 volts (see (a) under values of A_1 above) can be explained, since the rough crystalline surface of the hydride scum at the edge of the pool would increase the effective area of that part of the surface. The one discrepancy with the view that the KH is responsible for the ϕ of 1.3 volts is that the *C* currents under certain conditions gave a value of ϕ as high as 2.2 volts. This occurred after heating to unusually high temperatures and was probably due to the KH scum dissolving in the potassium.

In as much as the KH appears to be the source of the currents, and since this compound was decomposing under the conditions under which the currents were measured (the decomposition pressure was given as 0.10 mm Hg at 215°C[5] which is far higher than that existing during current measurement) it seems likely that the emission was due to the decomposition of the KH, rather than being of truly thermionic origin. Direct evidence for this view was obtained on one run during which the mercury cut off was closed and the gas was allowed to accumulate. It was found that the *D* current (no measurements made on *C* current) was proportional to the rate of gas evolution as would be expected on such a basis. Furthermore, the wide variation in the constant A_1 from 10^{-3} to 10^{3} times the "normal" value would fit in better with a decomposition phenomenon than a thermionic one.

A word may be said with regard to the reason for Fredenhagen's currents being so much smaller (see Table I) than those observed by Richardson and Young in spite of his poorer vacuum conditons. Assuming that the magnitude of the currents depends on the amount of KH present, the important factors in reducing an initially large current are temperature and time of heating, and not the value of the pressure, provided that this is below the decomposition pressure of the KH at the heating temperature. Due to the large value of this decomposition pressure (see above) it is easily seen that Fredenhagen's procedure should be more efficient in reducing the currents than that of Richardson and Young.

The very small current (see Table I, 14) found by Richardson and Young on one occasion just after the potassium was introduced into the apparatus might be accounted for by assuming that the hydride generally encountered in such experiments is formed from hydrogen set free by the breaking down of hydrocarbon vapors dissolved in the potassium. Hence some heating of the potassium would be necessary for the formation of the KH, and indeed these observers found their usual current values after several heatings of the potassium in their apparatus.

The author wishes to acknowledge his very great indebtedness to Drs. C. E. Mendenhall and R. C. Williamson, under whose direction this work was carried out.

EFFICIENCY OF EXCITATION BY ELECTRON IMPACT AND ANOMALOUS SCATTERING IN MERCURY VAPOR

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Abstract

The efficiency of excitation by electron impact of the 6.67 volt resonance level in the mercury atom has been studied as a function of the energy of the incident electrons. The electrons that have lost energy are separated out by a small retarding field and measured. The number of collisions is calculated from the experimentally determined value of the mean free path. The range covered is 0.4 volt from 6.67 to 7.07 giving a value for every 0.1 volt of the interval. The efficiency reaches a maximum of about 0.06 at 6.77 volts and then falls off to 0.04 at 7.0 volts.

The number of electrons scattered elastically at large angles by mercury vapor as a function of their energy was measured. The energy range covered was from 2 to 10 volts in steps of 0.2 of a volt. Certain very definite singularities were found. These correspond to an increase in large angle scattering and occur most prominently at 4.9, 5.7, and 6.3 volts. A less prominent group of singularities was also observed at 9.6, 10.3 and 11.1 volts.

Introduction

WHEN electrons travelling with a given velocity traverse a region occupied by a gas or vapor, two types of collisions can result. One type termed elastic collision refers to a process in which the electron on approaching the vicinity of an atom, suffers a change in direction but loses to the atom little or none of its energy. The other type known as an inelastic collision is characterized by the fact that the electron transfers to the atom all or nearly all of its energy. This transfer of energy can ionize or excite the atom. The necessary condition that an electron can suffer such a collision is that it have an energy greater than or equal to the ionization or excitation energy of the atom involved.

Franck and Einsporn[1] experimentally determined the critical potentials for electrons in mercury vapor. These critical potentials were exceptionally well checked in later work by Helen Messenger.[2]

Other experimenters have measured the absorption coefficient of mercury vapor for electrons as a function of the velocity of the electrons. This was done by Brode,[3] Maxwell,[4] and Jones.[5] These measurements necessitate the definition of a collision between an electron and an atom. The experiments were of two types. One defines a collision of an electron and an atom as any process that will remove an electron from the original beam by a change in

[1] Franck and Einsporn, Zeits. f. Physik **2**, 18 (1920).
[2] H. Messenger, Phys. Rev. **28**, 962 (1926).
[3] R. B. Brode, Proc. Roy. Soc. **109A**, 937 (1925).
[4] L. R. Maxwell, Proc. Nat. Acad. Sci. **12**, 509 (1926)
[5] T. J. Jones, Phys. Rev. **32**, 459 (1928).

direction. The other by nature of the experiment necessitates the removal of the electron from the beam if it suffers either a change in direction or a loss in energy. Both types of experiment give the same order of magnitude for the value of the absorption coefficient.

This presents another problem. If we take the values of the absorption coefficient (as experimentally determined in the work above) and calculate the fraction of the electrons that collide with atoms, what fraction (of the above fraction) lose energy when the electrons have a given velocity or energy? This may be called the efficiency of the process or, on the other hand, might be looked upon as the ratio of the collision area of the atom for excitation to the collision area of the atom as determined above from mean free path experiments.

Sponer[6] investigated the excitation of the mercury atom by electrons having velocities between 5 and 6 volts. She found an average efficiency for this range of 0.004. Hertz[7] recalculated her results taking a different value for the total number of collisions and obtained 0.03 for the average efficiency. These calculations were based on the kinetic theory value for the mean free path of the electron.

Eldridge[8] determined the relative probabilities of excitation of some of the important critical potentials in mercury vapor. He found evidence for loss in energy of the electrons corresponding to 4.9 volts as soon as the electrons have a velocity equivalent to 4.9 volts and that the efficiency of this process decreases as the velocity of the electrons is increased from this point on. He finds no evidence for a loss of energy of 6.7 volts when the incident electrons have energies corresponding to 6.7 volts but as the energy of the electrons increases the probability of excitation of 6.7 increases until it is quite pronounced.

Dymond[9] investigated the efficiency of excitation of the 19.77 volt level in the helium atom. He found that the efficiency increased to a maximum at about 0.25 of a volt above the critical potential and then decreased. The absolute magnitude of the maximum was found to be about one-tenth of one percent.

Glockler[10] has investigated the efficiency of excitation of the 19.77 volt level in helium by electron impact. He arrives at his conclusions by a study of the effect these inelastic collisions have on the current voltage characteristics of the experimental tube. He finds that the efficiency must rise to a maximum at about 0.2 of a volt after 19.77 and then falls off rapidly. He finds a maximum efficiency of 0.002.

This paper naturally divides itself into two parts. The first part is the description of an attempt by the writer to calculate the absolute efficiency of excitation by electron impact of the 6.7 volt energy level in the mercury

[6] H. Sponer, Zeits. f. Physik **7**, 185 (1921).
[7] G. Hertz, Zeits. f. Physik **32**, 298 (1925).
[8] Eldridge, Phys. Rev. **20**, 456 (1922).
[9] G. Dymond, Proc. Roy. Soc. London **107**, 291 (1925).
[10] G. Glockler, Phys. Rev. **33**, 175 (1929).

atom. The second part is the account of a study of the current-voltage characteristics of the tube and describes some conclusions arrived at as a result of this study.

Experimental Arrangement

The arrangement is shown diagrammatically in Fig. 1. Electrons from a hot tungsten filament were allowed to diffuse through the first diaphragm. They were accelerated by a given field between the first and second diaphragm. The third diaphragm was kept at the same potential as the second diaphragm. The electron beam defined by these diaphragms passed into the region inclosed by cylinders 1 and 2. The diameters of the diaphragms were 3 mm.

Some question was raised as to the possible effect of emission of secondary electrons from the walls of the first cylinder. The rings as shown were introduced to make cylinder 1 a better collector but this did not change the current-voltage characteristics of the tube thus indicating that the effect of such secondary emission was negligible.

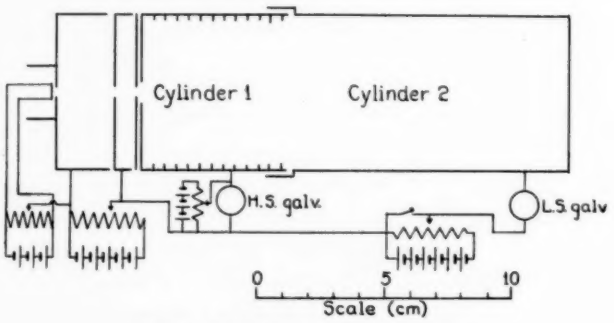

Fig. 1. Experimental arrangement.

Except for the filament, the tube was made of copper. The surfaces surrounding the diaphragms and the inside of the cylinders were coated with a thin layer of soot.

The arrangement was such that the electron stream was shielded from insulating surfaces on which charges might build up. All metal parts including the layer of soot were baked out to red heat under vacuum in an auxiliary vacuum furnace. They were then assembled in the final Pyrex tube where they were finally baked out at 500°C before the filament was lighted. Ground glass joints were used. They were covered on the outside by hard wax. The pressure inside could be maintained better than 10^{-4} mm of mercury for weeks at a time without running the pumps. Actually, when runs were taken the pumps were kept running. The tube was allowed to remain at room temperature and a mercury vapor trap was always kept at a temperature less than that of the room.

The earth's field was balanced out in the region occupied by the tube by the use of large Helmholtz coils.

It is to be noticed that the conditions under which this work was done were such that the mean free path of the electrons was of the same order of magnitude as the dimensions of the tube and that the current density was low. Total current was of the order of magnitude of 5×10^{-8} amperes.

These conditions are very different from the conditions generally present when critical potential measurements are made which are, high current density and short mean free path for the electrons.

Efficiency of Excitation

Let $f(v)dv$ be the fractional number of electrons having velocities between v and $v+dv$ where v is in volts. Let $\phi(v)$ be the chance that an electron having a velocity v will lose an amount of energy corresponding to a voltage drop of a if it collides with an atom. Let $C(v)$ be the fractional number of electrons that collide with atoms in a distance x when the electrons have a velocity corresponding to a voltage drop of v. Let $N(v)$ be the total number of electrons when the voltage drop is v. Then

$$n(v)dv=\phi(v)f(v)C(v)N(v)dv \tag{1}$$

where $n(v)dv$ is the total number of electrons that have lost energy in the interval v to $v+dv$.

Now if we can measure $n(v)\delta v$ the total number of electrons that have lost energy in the interval v to $v+\delta v$ where δv is a finite interval then we have

$$\phi(v)=\frac{n(v)\delta v}{N(v)f(v)C(v)\delta v} \tag{2}$$

where $\phi(v)$ is the average efficiency of excitation for the finite interval v to $v\pm\delta v$.

Now in order to determine the efficiency of excitation of the 6.67 volt energy level in the mercury atom we must measure the total current or the total effective number of electrons, the velocity distribution of the electrons, the number of collisions that these electrons make in a certain distance and the number of the electrons that lose 6.67 volts equivalent energy in this distance.

The experimental procedure was as follows: a galvanometer was connected to cylinder 2, and a very high sensitivity galvanometer was connected to cylinder 1. If we measure the current to cylinder 2 with retarding field and without retarding field at a particular voltage, the difference will give the number of electrons stopped by the retarding field. Also it does not matter whether we measure the change in the current to cylinder 2 or cylinder 1, as the geometry of the experimental arrangement is such that a decrease in current to cylinder 2 must be compensated by a corresponding increase to cylinder 1. Actually a high sensitivity galvanometer was connected to cylinder 1. The scattered current to cylinder 1 was balanced out by a counter e.m.f. across the galvanometer and only the difference in currents with retarding field on and off was measured.

Two runs were taken varying the accelerating voltage by steps of a tenth of a volt (Table I). At each value of the accelerating voltage, the current to the second cylinder was read, a reading on the high sensitivity galvanometer connected to cylinder 1 was taken, the retarding potential of a tenth of a volt was applied and the high sensitivity galvanometer was read again, the retarding potential was removed and the first reading on the high sensitivity galvanometer was checked. After this the accelerating voltage was moved up step by step, taking these readings at every step. Other runs were taken

TABLE I. *Sample data from runs 1 and 2 taken at a pressure of mercury vapor 0.0006 mm. V_a is the accelerating potential, i_t the total current, Δi_1 the difference between the current to cylinder 1 with and without the retarding potential of 0.1 volt, i_r the residual current, $C(v)$ the chance of collision.*

V_a	i_t	Δi_1	$\Delta i_1/i_t$ $\times 10^3$ run 1	$\Delta i_1/i_t$ $\times 10^3$ run 2	Ave. $\Delta i_1/i_t$ $\times 10^3$	i_r/i_t $\times 10^3$	Diff. $\times 10^3$	$\div C(v)$	Same $p=0.0014$ mm
4.1	364	0.6	1.65	2.32	1.98				
4.2	369	1.0	2.71	2.78	2.74				
4.3	375	1.0	2.67	2.48	2.57				
4.4	380	0.8	2.13	2.44	2.28				
4.5	386	0.7	1.81	2.40	2.10				
4.6	390	0.6	1.54	1.42	1.48	1.20	0.28	0.00131	0.00144
4.7	396	0.8	2.02	1.65	1.83	1.18	0.65	0.00305	0.00186
4.8	403	1.2	2.97	2.31	2.64	1.16	1.48	0.00686	0.00645
4.9	407	1.4	3.44	2.95	3.19	1.14	2.05	0.00964	0.00965
5.0	411	1.3	3.16	3.38	3.27	1.11	2.16	0.01015	0.01010
5.1	417	1.1	2.64	2.66	2.65	1.09	1.56	0.00733	0.00801
5.2	419	1.0	2.38	2.30	2.34	1.07	1.27	0.00597	0.00585
5.3	423	1.1	2.60	2.28	2.44	1.05	1.39	0.00653	0.00493
5.4	429	0.8	1.87	1.92	1.89	1.03	0.86	0.00404	0.00510
5.5	434	0.9	2.07	1.69	1.88	1.01	0.87	0.00408	0.00373
5.6	439	0.6	1.37	1.45	1.41	0.99	0.42	0.00197	0.00331
5.7	444	0.6	1.35	1.23	1.29	0.91	0.33	0.00155	0.00280
5.8	448	0.7	1.56	1.42	1.49				
5.9	453	0.6	1.33	1.61	1.47				
6.0	458	0.8	1.43	1.39	1.41				

from time to time, measuring the current to cylinder 2 and the total current to both cylinders. From these data, the total current can be computed for any other run, provided we know the current to cylinder 2. In the case of the two runs we are considering, the readings on the high sensitivity galvanometer were differenced, giving the current stopped by the retarding potential of a tenth of a volt.

The total current was computed and was multiplied by the ratio of sensitivity of the two galvanometers, and the current stopped by the retarding field was divided by this, giving the fraction of the total current stopped. These results for the two runs (taken on different days) were averaged and their plot against accelerating voltage is that given in Fig. 2. This process was then repeated for retarding fields of 0.2, 0.3, 0.4, 0.5 and 0.6 of a volt respectively. Two complete sets of runs were taken at pressures of mercury vapor corresponding to temperatures of 13°C and 22°C respectively.

The electrons stopped by the retarding field may be divided into two groups: first, electrons scattered elastically at large angles will be stopped if

their velocity component in the direction of the field, is too small to cross the retarding field; and second, some of the electrons that have lost energy in collision will be stopped by the retarding field. In Fig. 2 we have peaks superimposed on a residual current. The residual current is due to the first group, and the peaks to the second group.

In order to determine the energy loss to which each peak corresponds, we must know the voltage correction in the tube. By analyzing the peaks that occur in runs taken over a large range of accelerating voltages and by determining voltage at which ionization of the mercury vapor sets in, it was found that the voltage correction was approximately 1.8 volts. On this basis the second and largest peak in Fig. 2 is due to electrons that have lost 6.67 volts energy.

The number of electrons that, having lost energy, are subsequently stopped by the retarding field, will depend on three things; first, the direction

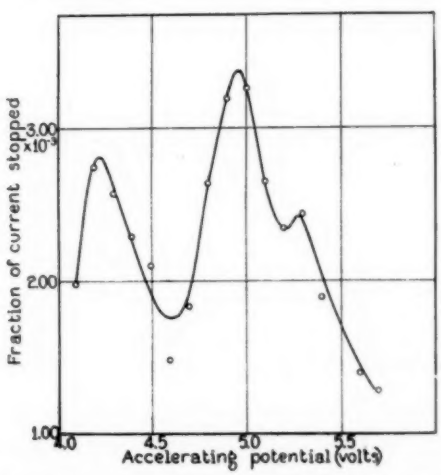

Fig. 2. Fraction of the total current stopped by a retarding potential of 0.1 volt. Mercury vapor pressure 0.0006 mm.

of their motion after inelastic collision; second, the amount of energy that they have left; and third, the potential difference between the second cylinder, and the point where the collision occurred.

For the purpose of this calculation, the writer feels justified in the assumption that the average angle of scattering on inelastic collision was small. No definite proof that this is so for the low velocities in this experiment was found, but indications from the study of current-voltage characteristics of the tube, pointed strongly to the fact that this assumption was correct. For instance, energy losses could be detected in the electron stream, entering cylinder 1 from the last diaphragm. The magnitude of these energy losses indicated that most of the electrons that lost energy while passing through the diaphragms continued straight on so as to come through the last diaphragm. On the basis of this assumption, it may then be said that the number of electrons stopped, over and above the residual current as

measured by the second peak for the case where the retarding potential was one-tenth of a volt, is a measure of the number of electrons that have lost energy, having a velocity to start with between 6.67 volts and 6.77 volts. (Fig. 2.)

In order to estimate the value of the residual current, runs similar to those described above were taken starting in at 2 volts and ending at 10 volts. From a plot of these results the residual current can be determined approximately and subtracted out. We then have left in Fig. 3 the electrons that

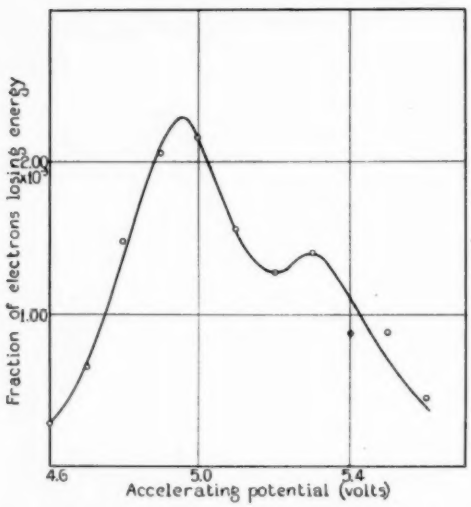

Fig. 3. Fraction of electrons that have lost energy due to inelastic collision, retarding field 0.1 volt, mercury vapor pressure 0.0006 mm.

have lost 6.7 volts energy when a retarding potential of 0.1 volt was applied.

Referring back to the theoretical development we now have

$$n(v)\delta v/N(v).$$

Now consider the two sets of runs for the two pressures of mercury vapor, 0.0014 and 0.0006 mm. If we knew $C(v)$ for both pressures we would have

$$\left[\frac{n(v)\delta)}{N(v)C(v)}\right]_{p_1} = \left[\frac{n(v)\delta v}{N(v)C(v)}\right]_{p_2}$$

where $C(v)$ is the fraction that have collided:

$$C(v) = I/I_0 = 1 - e^{-\alpha p x}$$

where x is the effective distance, α the effective cross section in cm^2/cm^3, and p the pressure in mm of mercury. We know p and from work of Jones,[5] Maxwell,[4] and Brode[3] α is approximately 100. This value is taken between 4 and 5 volts on Jones' curve. That this is the right point is shown by comparison of results in Jones' tube and the writer's tube.

The length of the first cylinder is 5.5 cm but there is good reason to doubt that this whole length is effective. To satisfy Eq. (3) it is necessary to take x

equal to 4 cm. This value of x was used as the approximate value of the effective distance. If we took 5 cm or 5.5 cm the results for the two pressures would not agree as well and the resulting efficiency would be decreased by a factor of 0.85 or 0.70 respectively.

Now that the choice of x is made the two sets of data can be corrected for pressure and corresponding curves averaged together. We then have a loss in energy curve for each value of the retarding potential.

The velocity distribution was determined by connecting cylinders 1 and 2 together and putting them at a negative potential of 6.67 volts with respect to the last diaphragm. The mercury vapor was frozen out with liquid air. The accelerating voltage was then varied in steps of a tenth of a volt measuring at each step the current to cylinders 1 and 2. The total current to cylinders 1 and 2 without retarding field was also measured at each step. The ratio of the current to the cylinders with retarding field applied to the total current gives the fractional number of electrons that had velocities great

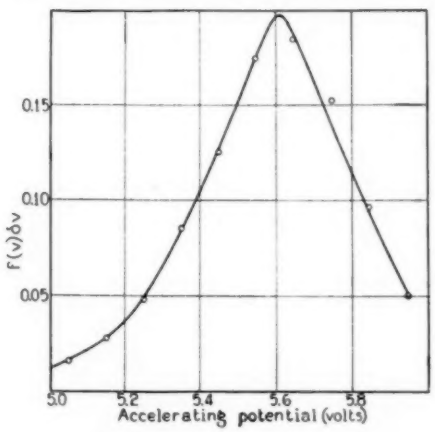

Fig. 4. Velocity distribution.

enough to cross the field. The plot of these values would give the integral of the velocity distribution. If we take the differences between successive values and divide by the interval (one-tenth volt) we have approximate values for the velocity distribution. If we do not divide by the interval we have $f(v)\delta v$ which is the quantity we wish to use in our calculations.

If we fit the values of $f(v)\delta v$ as shown in Fig. 4 to the values of $n(v)\delta v/N(v)C(v)$, as is done in Table II, and divide by corresponding values of $f(v)\delta v$ we get in each case a result for the average efficiency of excitation of 6.67 for electrons that had presumably velocities between 6.67 and 6.77 volts energy before colliding. Averaging these values we get an efficiency of 5.5 percent. The reason for considering only values of $n(v)\delta v/N(v)C(v)$ near the peak of the curve is that these are undoubtedly the most accurate.

Now in going on with the calculation we have two methods. One method would be to subtract from the curve for retarding potential $v_r=0.2$ the curve for $v_r=0.1$. This would introduce into the second calculation experimental

deviations in the first curve besides the experimental deviations already in the second. A second method would be to take 5.5 percent as the best value we have and, using the curve for $f(v)\delta v$, reconstruct the curve for $[n(v)\delta v/N(v)C(v)]$. The velocity distribution $f(v)\delta v$ is capable of fairly

TABLE II. *Completion of calculation for efficiency of excitation of the 6.67 level for electrons having velocities between 6.67 and 6.77.*

Accelerating voltage	Average of last two col Table I	Velocity distribution	Ratio	Average of ratio	Reconstructed curve
4.6	0.00137				0.0026
4.7	.00245				.0047
4.8	.00665	0.124	0.054		.0068
4.9	.00964	.173	.056		.0095
5.0	.01012	.184	.055		.0101
5.1	.00767	.152	.050	.055	.0084
5.2	.00591	.096	.062	——	.0053
5.3	.00573				.0028
5.4	.00457				.0017
5.5	.00390				
5.6	.00264				
5.7	.00217				

accurate determination. The second method appears to the writer to be the best. This procedure gives 5.5 percent as the efficiency of excitation of 6.67 by electrons having energies between 6.77 and 6.87 volts before they collided. Reconstructing again and proceeding in the same way, we get the values 4.8 and 4.1 percent respectively for electrons having energies between 6.87

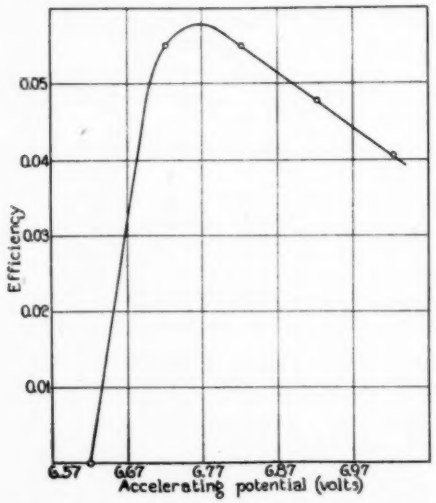

Fig. 5. Efficiency of excitation of the 6.67 volt energy level as a function of the velocity of the electrons.

and 6.97, and 6.97 and 7.07 before colliding. Carrying this procedure on to data obtained from retarding potentials of 0.5 and 0.6 volt meant very little, probably due to effect of another critical potential above 6.67. Fig. 5 shows these efficiencies plotted against accelerating voltage.

The position of the maximum of the curve for $f(v)\delta v$ on the accelerating voltage scale, Fig. 4, does not agree with the position of the maximum of $n(v)\delta v/N(v)C(v)$ in Fig. 3. The velocity distribution was determined by applying a retarding field between cylinders 1 and 2, connected together, and the electron gun. The ratio $n(v)\delta v/N(v)C(v)$ was obtained by applying a retarding field between cylinders 1 and 2. Measurement of critical potentials at both points showed a corresponding shift in the peaks. This is probably due to the action of a contact e.m.f. Therefore $f(v)\delta v$ was fitted to $n(v)\delta v/N(v)C(v)$ and moved up a tenth of a volt for each successive calculation.

As to the absolute value, this involves the choice of x and the direction the loss in energy electrons take after losing energy. If many electrons, after losing energy, are scattered at large angles, a drawing-out field on cylinder 2 should give some indication of this, and it does, but less than 25 percent of the effect with a retarding field. As for x, it cannot be much longer than 5 cm, which would mean a reduction of 15 percent, and if it were as short as 2 cm an increase of, roughly, 50 percent. A fair statement would be to say that the maximum average efficiency in any tenth volt interval near 6.7 was less than 20 and greater than 3 percent, and very probably between 5 and 15 percent.

It should be remarked that the present experiments have nothing to say about the efficiency of excitation of the 6.7 volt level by electrons having speeds in excess of that corresponding to about 7 volts. It is entirely possible, and studies of the intensity of 1849 in emission seem to indicate, that the efficiency of excitation of this level rises to a general maximum in the neighborhood of 15 volts. The present experiments merely indicate that this rise is not a smooth one but that there is at least one subsidiary maximum close to the critical potential.

Anomalous Scattering

From a study of the current arriving at cylinders 1 and 2 (both cylinders at the same potential) as a function of the accelerating voltage certain singularities or irregularities have been found.

On the basis of the fact that the mean free path of the electrons in mercury vapor increases with increasing accelerating voltage the fraction of the total current reaching cylinder 1 should fall off with increasing accelerating potential and the fraction of the total current reaching cylinder 2 should likewise increase. It would at first seem reasonable that this variation should be smooth and gradual.

It has been found that this is not entirely the case. Such curves as are shown in Fig. 6 are persistently obtained. This behavior might be due to a number of things besides the mercury vapor in the tube. To test this the mercury vapor was frozen out with liquid air. The curves obtained under this condition were always smooth. As a further test helium was introduced into the tube with liquid air still on the trap. In this case the curves were smooth in the region from 0 to 10 volts accelerating potential but in the

neighborhood of 20 volts singularities again appeared. It seems that this is very good proof that the singularities are a function of the gas in the tube.

Very little is known about the exact mechanism of the collisions between electrons and atoms as a function of the velocity of the electrons. Elasser[11] has calculated the absorption coefficient for slow electrons in atomic hydrogen up to and including the effect of the first resonance line. He finds an anomalous increase in the absorption coefficient at about the voltage corresponding to this resonance line. If he included other lines of the hydrogen spectrum in his calculations, might he not get other singularities?

Experimentally such singularities have been found by the writer in mercury vapor. In order to bring them out the high sensitivity galvanometer connected by cylinder 1 was used. The curve showing the variation of the current scattered to cylinder 1 as a function of the applied accelerating

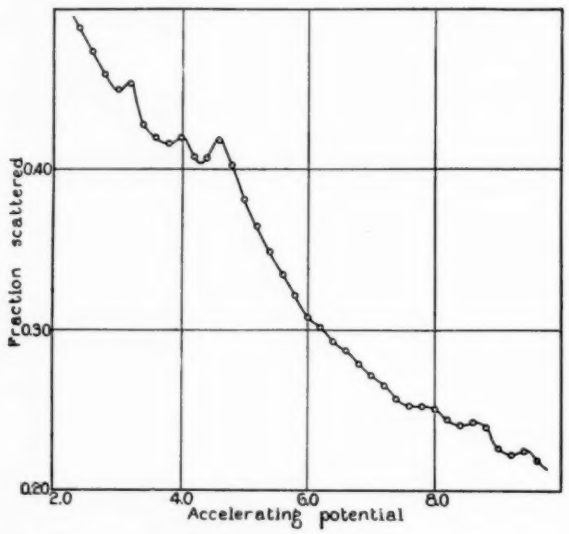

Fig. 6. Ratio of current scattered to cylinder 1 to the total current as a function of the speed of the electrons.

potential is shown in Fig. 6. The slope of this curve plotted on a voltage scale corrected for initial velocity is given in Fig. 7. It is an average of two separate runs that agreed very satisfactorily.

It should be pointed out that the singularities here observed are not due to inelastic collisions for these are relatively much too infrequent to produce the effects observed. The effects are due to rather abrupt increases, at certain critical potentials, of the number of electrons scattered by the mercury atoms through large angles. The relation of these potentials to the usual critical potentials of the mercury atom is uncertain. Excess scattering reaches a maximum at potentials (corrected) of 4.9, 5.7 and 6.3 volts; and again, though less pronounced, at 9.7, 10.3 and 11.1 volts. Between these two

[11] Elasser, Zeits. f. Physik **45**, 522 (1927).

groups are minor irregularities which are not prominent enough to allow one to attach to them much significance. It may be significant that there is a nearly constant difference of 4.8 volts between the corresponding maxima of the two groups.

It should be pointed out that the most prominent group of singularities accounts for the irregularity found in the mean free paths of electrons in

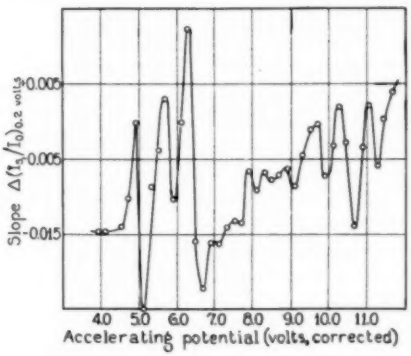

Fig. 7. Slope of the curve of Fig. 6.

mercury vapor by Maxwell[5] and Jones.[6] They are probably to be correlated with the maxima in the absorption coefficients for electrons in the vapors of the alkali metals which Brode[12] has recently found in the vicinity of the critical potentials of those metals.

In conclusion the writer wishes to express his appreciation for the advice of Professor John T. Tate under whose direction this work was carried out.

[12] Brode, Phys. Rev. **33**, 1069 (1929).

THE DISTRIBUTION OF ELECTRONS BETWEEN THE PLATE AND GRID OF A THREE ELECTRODE TUBE AS DETERMINED BY POSITIVE CAESIUM IONS

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(Received May 13, 1929)

Abstract

Number of electrons emitted from a Cs covered surface per positive Cs ion. The source of the ions was a tungsten filament maintained at about 1200°K in the bulb of a radiotron UX201A containing caesium vapor. The plate current and positive ion current emitted from the filament were observed for each of several negative grid potentials as the plate potential was varied from +45 to −600 volts. From these observations the number of electrons that was emitted from the caesium-covered grid per positive ion was calculated. The number increased uniformly from zero at about 95 volts to 0.24 at 600 volts.

Calibration of tube. After corrections for the emission of secondary electrons from grid and plate were made, the ratio of the positive ion current to the plate to the positive ion emission from the filament was found to increase to 0.86 as the ratio of the plate potential to the grid potential reached 0.75. Beyond this point the relative distribution of positive ions remained constant for all ratios of plate to grid potential. This fraction 0.86, is the same as the ratio between the total area of a surface in the plane of the grid and the actual area of the grid as seen from the filament. Assuming the same distribution of electrons as positive ions, the fraction of the electrons reaching grid and plate in this type of tube may be calculated from the grid dimensions provided the plate potential is greater than 0.75 of that of the grid.

Introduction

In A previous report[1] the writer described experiments which led to the determination of the relative distrubution of positive caesium ions between the cylindrical plate and grid of a three-electrode tube. It was also shown that the fraction of positive ions caught by the grid and plate respectively was proportional to the area of the solid and the open portions of the grid. It can be shown theoretically that the paths of positive ions in a tube of this type are the same as those of electrons at the same accelerating voltage. Hence it was assumed that with positive voltages of grid and plate the fraction of electrons caught by the plate would be measured by the ratio of the projected area on the plate of the open portion of the grid to the total plate-area.

The material presented in this paper describes similar experiments with a plane-anode type of tube.

Apparatus

The tube was a standard radiotron UX201A with a pure tungsten filament, which was the source of positive caesium ions when maintained at a

[1] Hyatt, Phys. Rev. **32**, 922 (1928).

temperature of about 1200°K.[2] A diagram of the tube and electrical connections is shown in Fig. 1. The tube was evacuated by a mercury vapor pump backed by an oil pump. A trap was immersed in liquid air during the exhaust. The tube was baked out at about 200°C while the pumps were running. A higher temperature bakeout often resulted in leakage currents across the stem after the caesium had been distilled into the tube. The plate was heated by induction until all evidence of emitted gases had disappeared.

Caesium was generated by heating by induction a metal capsule containing a mixture of caesium chloride and calcium. The experimental tube was then sealed off from the pumping system and tested.

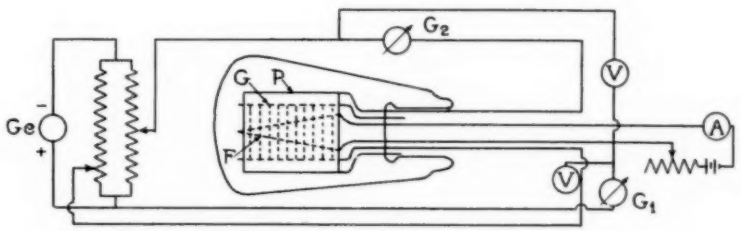

Fig. 1. Diagram of tube and electrical connections.

The filament was heated by the current from a storage battery and the grid and plate potentials were maintained by a motor generator set, *Ge*. The positive ion emission from the filament which was approximately two microamperes at the existing caesium vapor pressure was measured by a galvanometer, G_1. A galvanometer, G_2, in the filament-plate circuit indicated the total plate current.

Experimental Procedure

The experiments were carried on while the tube was immersed in a water bath maintained at about 30°C in order to hold the pressure of the caesium vapor constant. The grid and plate were covered with at least a monatomic layer of caesium throughout the experiments.

The positive ion emission from the filament and the plate current were observed as the plate potential was varied from +45 to −600 volts with respect to the positive end of the filament, while the grid potential was maintained constant at each of the values, −125, −250, −360 and −500 volts.

Results

While the plate potential was varied from +45 to 0, the plate current was nearly constant and consisted of electrons which were emitted from the caesium covered grid by the bombardment of positive ions. This is shown by the part of the curve below the axis of abscissas in Fig. 2. At these plate potentials it was assumed that all the positive ions were collected by the grid. The electron current to the plate divided by the positive ion current

[2] Langmuir and Kingdon, Science **57**, 58 (1923).

from the filament gives the number of secondary electrons per positive ion on the grid. This ratio for various accelerating grid potentials with the plate

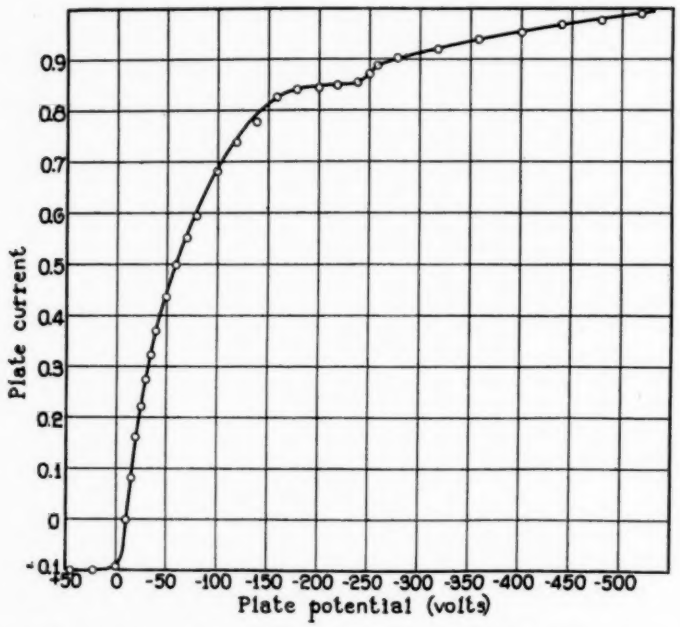

Fig. 2. Total plate current as a function of plate potential with grid at −250 volts. Positive ordinates indicate an excess of positive ions to the plate, negative ordinates indicate an electron current from grid to plate.

maintained at +45 is shown by Curve I in Fig. 3. The curve indicates that the emission of secondary electrons starts at about 95 volts and that the

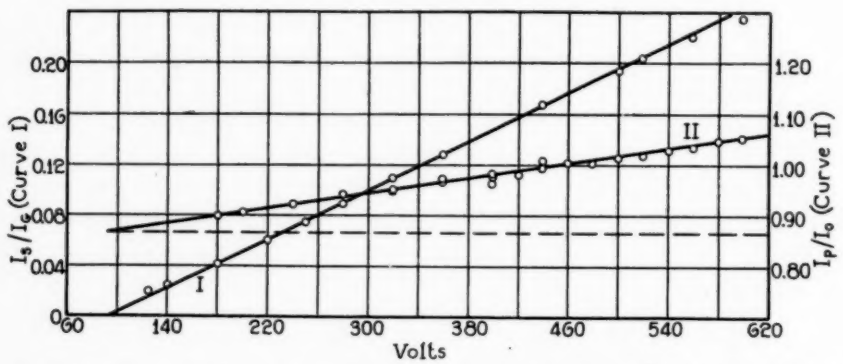

Fig. 3. Curve I. Number of secondary electrons from the grid per positive ion at the grid as a function of the grid potential. Curve II. Total plate current in terms of unit positive ion emission from the filament as a function of the plate potential for values of E_p/E_g greater than unity.

number of secondary electrons per positive ion increases uniformly with the accelerating potential.

As the plate potential was made negative for a fixed negative grid potential, the plate current reversed because the plate began to collect positive ions in addition to the electrons from the grid. This is shown by the curve in Fig. 2. The ordinates represent the plate current, I_p, and the abscissas represent the plate potential, E_p. The grid potential, E_g, was held at -250 volts. I_p increases rather rapidly up to -150 volts and then changes but little until a potential a little less than -250 is reached. At this point there is a sudden increase in I_p which is followed by a uniform change as E_p increases. The plate current for values of E_p less than E_g is made up of positive ions from the filament and secondary electrons from the grid. As the ratio of the plate to grid potential passes unity, the plate ceases to collect secondary electrons from the grid and begins to lose them to the grid and filament. The increase in I_p as the plate is made more negative than the grid indicates that the number of secondary electrons from the plate increases as the positive ion speed increases.

The ratio of the plate current, I_p, to the total emission current from the filament, I_0, is plotted as ordinates, and the ratio of the plate potential, E_p, to the grid potential, E_g, is plotted as abscissas in Fig. 4 for each of several grid potentials. The values of I_p/I_0, for each grid potential, increase until E_p/E_g reaches about 0.75 and then remain nearly constant until E_p/E_g becomes unity. For values of E_p/E_g greater than unity there is a nearly uniform increase in I_p/I_0.

Fraction of Positive Ions Striking Grid and Plate

The actual positive ion current to the plate may be calculated from the data in Figs. 3 and 4 as follows: Consider the curve in Fig. 4 for E_g -250 volts. The difference between the ordinate 1 and the values of I_p/I_0 represents the fraction of the total current that reaches the grid. Below values of E_p/E_g equal to unity, the grid current is made up of positive ions from the filament and secondary electrons from the grid itself. If the grid current for values of E_p/E_g less than unity be multiplied by the value of the number of secondary electrons per positive ion at the grid obtained from the data of Curve I of Fig. 3, the result approximately represents the secondary electron current from grid to plate. This value is somewhat too large, since the grid current already included the secondary electrons emitted to the plate. If this calculated value of the secondary electron current from the grid be added to the observed plate current, we obtain an approximate value of the actual positive ion current to the plate. This current is a little too large because the grid current with which we started was too large. If the calculation is repeated, using the new value of the plate current we obtain the true value of the positive ion plate current for values of E_p/E_g less than unity.

It is probable that the number of secondary electrons from the plate per positive ion at the plate for a given plate potential is very nearly the same as that for the grid at the same potential. If this is assumed, it becomes possible to determine the fraction of the positive ions that reaches the plate for values of E_p/E_g greater than unity.

It was observed during the experiments that the emission current, I_0, suddenly increased as E_p/E_g passed through unity and then increased but little for larger values of E_p/E_g. This increase in I_0 was probably due to a few secondary electrons from the plate that were not caught by the grid, and to the secondary electrons from the grid that no longer go to the plate on account of the adverse field. The true positive ion emission from the filament for values of E_p/E_g greater than unity was then calculated by taking into account the above mentioned increase in the observed emission. If the observed plate current is now divided by this corrected value of the emission current larger ratios of I_p/I_0 are obtained.

The fraction of the total positive ion current reaching the plate for ratios of E_p/E_g above unity may be calculated as follows. The corrected values of

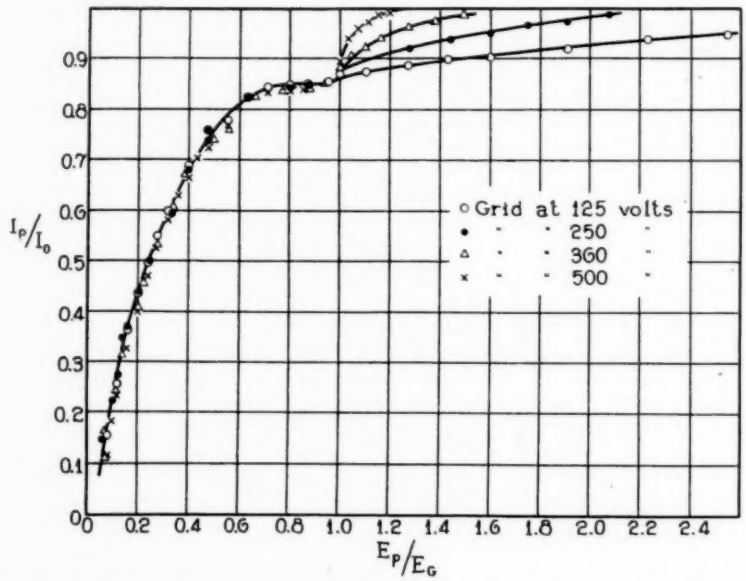

Fig. 4. Ratio of plate current, I_p, to the emission current, I_0, as a function of the ratio of the plate potential, E_p, to the grid potential, E_g.

I_p/I_0 are multiplied by the number of secondary electrons per positive ion at the grid according to Curve I in Fig. 3. This product is subtracted from the value of I_p/I_0 and is approximately the true fraction of positive ions that reach the plate. However, this value is a little too small for I_p/I_0 is larger than the actual fraction of positive ions to the plate. If the calculation is again made using the new value of I_p/I_0, we obtain a value which represents the fraction of the positive ions reaching the plate.

The same calculations have been applied to the curves in Fig. 4 for each grid potential and the resulting values of the fraction of the positive ions reaching the plate are in close agreement.

The plot shown in Fig. 5 represents the results obtained by making the calculations that have been described. The fraction F of the total positive

ion emission that reaches the plate is plotted as ordinates and the ratio E_p/E_g is plotted as abscissas for each of four grid potentials.

The fraction F increases to a value of 0.86 at a plate potential equal to 0.75 of the grid potential and then falls off by a little more than one percent as the plate reaches a potential twice that of the grid. The degree to which the results for values of E_p/E_g greater than unity conform to those for values less than unity justifies the assumptions that were made in the calculations.

However, the small decrease in F for the higher ratios of E_p/E_g suggests that the number of secondary electrons per positive ion at the plate is somewhat less than for the grid. This difference may be accounted for if a few of the positive ions from the filament go around the end of the plate and strike the back from which the secondary electrons would not be collected. The

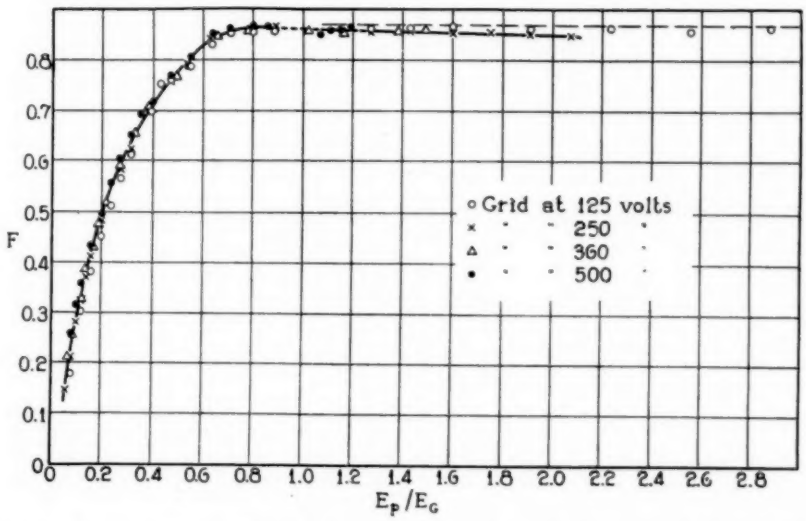

Fig. 5. Curves showing the fraction F of the total positive ion emission reaching the plate as a function of the ratio E_p/E_g while the grid of a tube was maintained at each of four potentials.

ends of the filaments in the tubes used did extend to the ends of the plate so it is probable that some of the ions did go around the ends to the back of the plate.

A second and probably less certain method of determining F for values of E_p/E_g greater than unity may be described as follows:

The values of I_p/I_0 shown by the curves in Fig. 4 were corrected for the increase in I_0 as E_p/E_g passed through unity as described above. These corrected values of I_p/I_0 are shown by Curve II in Fig. 3, where they are plotted as a function of the plate potential. The values of I_p/I_0 for the same plate potential but for different grid potentials fit together to give a good straight line. If the fraction of positive ions that strike the plate remains constant then the slope of this curve indicates the rate of increase of the number of secondary electrons per positive ion at the plate as the acceler-

ating potential increases. Curve I, Fig. 3 shows that secondary electron emission from the grid starts at about 95 volts. If it is assumed that secondary emission from the plate starts at the same accelerating potential, then the value of I_p/I_0, for Curve II, Fig. 3, corresponding to a plate potential of 95 volts, would represent the actual positive ion current to the plate in terms of unit emission from the filament. The ordinate on Curve II corresponding to 95 volts is 0.87. This is but little larger than the value of F obtained by the first method. The dashed line drawn at 0.87 for values of E_p/E_g greater than unity, in Fig. 5 indicates this value of F.

The plot shown in Fig. 6 shows the results obtained from four tubes of the UX201A type. The grid was maintained at -250 volts in each of the four cases.

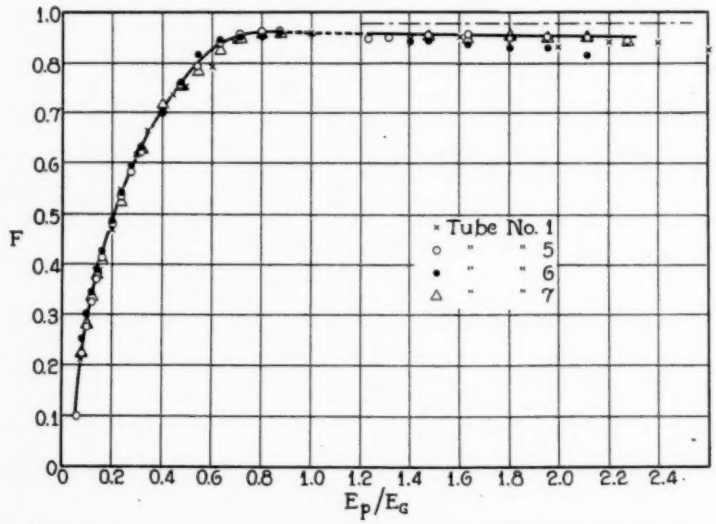

Fig. 6. The fraction F of the total positive ion emission reaching the plate as a function of the ratio E_p/E_g. Data from four tubes with the grid maintained at -250 volts.

It was anticipated, as in the experiment with the cylindrical anode tube previously reported, that the fraction of positive ions caught by the grid and plate respectively, would be the same as the ratio of solid to open parts of the grid. The area of the closed portion of the grid as seen from the filament and the total area of a surface in the plane of the grid were calculated for one of the tubes. The ratio of the closed area of the grid to the total area turns out to be 0.14 and the ratio of the open area to the total area is 0.86. This is nearly the same as the values of F shown in Figs. 5 and 6, for values of E_p/E_g greater than 0.75. Since it may be shown theoretically that electron paths are the same as the positive ion paths at the same potentials, it may be concluded that the shadowing or screening effect of the grid as regards the electron current to the plate may be calculated from the grid dimensions.

THE REFLECTION OF ATOMS FROM CRYSTALS

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(Received June 6, 1929)

Abstract

Beams of mercury, cadmium, and arsenic incident upon clean cleavage surfaces of rock-salt give rise to specularly reflected beams. Measurement shows that the velocity of the beam of cadmium atoms reflected from rock-salt may be represented by

$$\lambda=\frac{h}{mv}=2d\left(2.26-\frac{\phi}{\frac{1}{2}mv^2}-\cos^2\theta\right)^{1/2}.$$

A beam specularly reflected from a first crystal is specularly reflected at a second if incident upon it at the same angle at which reflection from the first took place. If the angles are nearly equal there is still some specular reflection at the second crystal but the intensity of the specular beam drops off with increasing difference of angles and the incident beam is scattered at random. A beam of cadmium atoms issuing from a boiler at 440°C and striking a rock-salt crystal at an angle of 45° gives rise to a specular beam containing about 17 percent of the incident atoms. The intensity of the beams specularly reflected at 22.5° and 67.5° are in the ratio 1:1.38. These facts indicate that associated with motion of translation of uncharged atoms and molecules there is a wave phenomenon of the type postulated by de Broglie.

THE fact that a beam of atoms incident upon a clean cleavage surface of a crystal may give rise to a well defined reflected beam making the same angle with the normal to the crystal surface as does the incident beam[1] suggests at once the wave-particle dualism exhibited in the Compton effect and the Davisson and Germer experiments. To understand this phenomenon in terms of the hard elastic spheres of Maxwell's kinetic theory or of the planetary atomic systems of Bohr is difficult, at least. On the other hand the wave, or, more properly superposition characteristics of the new quantum theory lead us at once to expect just such phenomena. Not in every case however does the incidence of an atomic beam upon a crystal surface give rise to a specularly reflected beam. We have already reported the existence of specularly reflected beams of mercury and cadmium from sodium chloride crystals and our failure to obtain specular reflection of sodium and atomic hydrogen.[2] We have since observed specular reflection of cadmium and arsenic beams from potassium chloride crystals and also of arsenic from sodium chloride, and have been unable to obtain specular reflection of either of these substances from orthoclase or flourite crystals. Arsenic vapour[3] is tetra-atomic at the temperature (ca. 250°C) at which we worked, so that specular reflection of molecules as well as of atoms is evidently possible.

[1] A. Ellett and H. F. Olson, Phys. Rev. **31**, 643 (1928).

[2] Johnson, Jour. Frank. Inst. **206**, 301 (1928) has since reported specular reflection of hydrogen from rock-salt.

[3] Landolt-Börnstein, Physikalisch-Chemische Tabellen.

If we consider the wave picture of de Broglie and Schroedinger then familiar phenomena of optics and the known behavior of electrons suggest that the specular reflection of atoms is analogous either to the Bragg type of x-ray reflection, or to reflection from a plane mirror, or from a plane grating. The experiments reported in the present paper appear to establish definitely the "wave" nature of the phenomenon, and to rule out the two latter possibilities. In brief we have been able to show; first, that a specularly reflected beam has acquired a property by virtue of which it is entirely specularly reflected from a second crystal only when incident upon that crystal at the same angle at which it was initially reflected, second, that a specularly reflected beam is made up of atoms all having very nearly the same velocity,

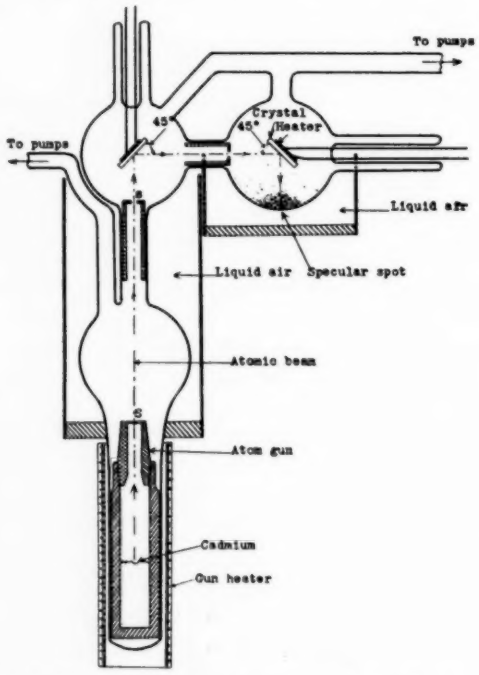

Fig. 1. Type of tube used for successive reflections.

and that this velocity varies with the angle of reflection in a characteristic way, third, that the intensity of the specularly reflected beam varies with the angle of reflection and that the ratio of intensities of the beams reflected at two angles is the ratio of the relative numbers of atoms in the incident beam having wave-lengths appropriate for reflection at these angles. These experiments will be taken up in the above order.

Reflection from two Crystals in Succession[4]

Figure 1 is a sketch of the apparatus used when the beam was reflected from the first crystal at an angle of 45°, and from it the method is evident.

[4] A preliminary report was read at the New York Meeting of the Physical Society, Phys. Rev. **33**, 124 (1929).

The results are presented graphically in Fig. 2, together with the velocities of the beams specularly reflected at the angles in question.

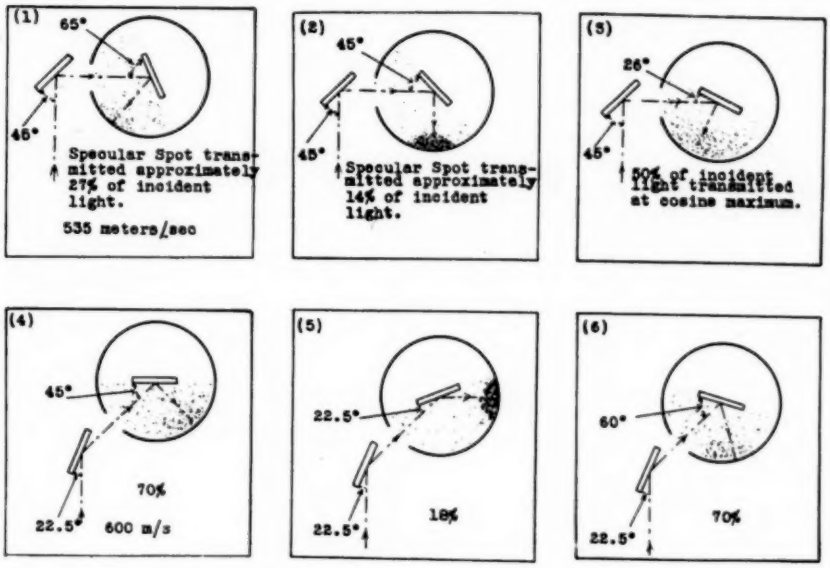

Fig. 2. Results of experiments on successive reflections.

Direct Measurement of the Velocity of Reflected Beams[5]

Figure 3 shows the apparatus, the method being that developed by Eldridge[6] for the experimental verification of the Maxwell distribution law. Atoms issuing from the slit S_1 pass through a second wide slit S_2 and impinge upon a

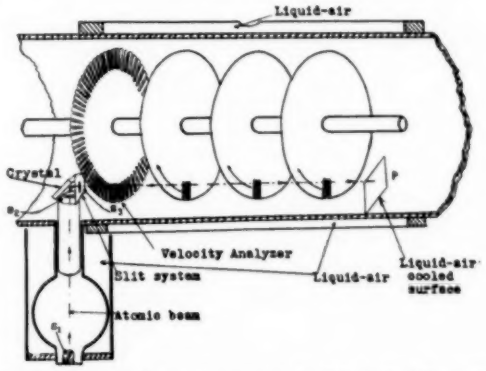

Fig. 3. Apparatus used to measure velocities of reflected atoms.

large area of the reflecting crystal. Part of the specularly reflected beam passes through the narrow slit S_3 and then those atoms which are moving in a direction appropriate to their velocity pass on through the rotating sectored

[5] A preliminary report appeared in Science, **68**, 89 (1928).
[6] J. A. Eldridge, Phys. Rev. **30**, 931 (1927).

disks and form a deposit upon the surface P. By rotating the disks first in one direction and then the other two deposits were formed. The plate P was then run through a microphotometer and the density of the deposits measured.

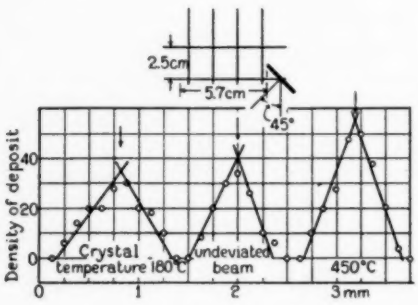

Fig. 4a. Speed of rotor, 72 r.p.s.; velocity of beam, 535m/s.

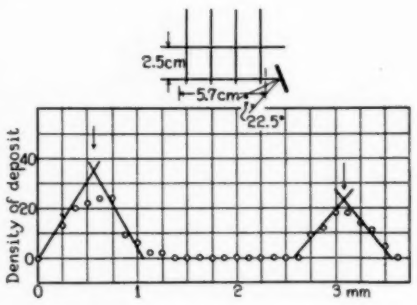

Fig. 4b. Speed of rotor, 73.5 r.p.s.; velocity of atom beam, 500m/s.

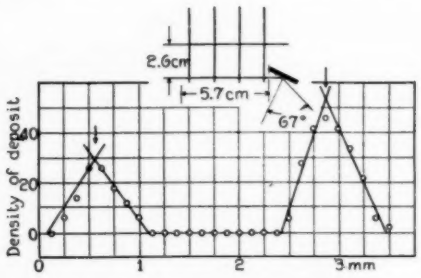

Fig. 4c. Speed of rotor, 76 r.p.s.; velocity of atom beam, 600m/s.

Fig. 4. Density curves obtained with apparatus shown in Fig. 3.

Densities were translated into relative numbers of cadmium atoms per unit area by the method described by Eldridge. Since the slit S_3 and the slits in

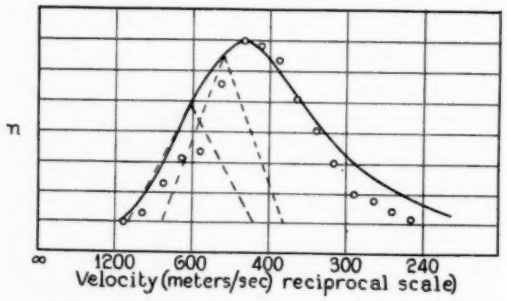

Fig. 5. Comparison of velocity distribution of cadmium atoms before and after reflection.

the sectored disks were the same width a beam of atoms having all the same velocity will form a deposit three times as wide as the slits with density varying linearly from zero at the edges to a maximum at the center.

The density curves obtained are shown in Fig. 4 (a, b, c), together with the rate of rotation of the sectored disks, the distance of the slit S_3 from the plate P, and the velocity corresponding to the observed separation of the deposits. It is evident from the inspection of these curves that the reflected beam of atoms contains only a narrow range of velocities, otherwise the deposits would not approximate so closely to the type to be expected for a purely monochromatic (single velocity) beam. Fig. 5 shows the deposit formed when the direct beam from the gun is incident upon the slit S_3. The heavy curve shows the distribution to be expected for a Maxwell distribution of velocities at the temperature of the gun, due allowance being made for the finite slit width of the velocity analyzer. The dotted triangles are the types of deposit obtained by reflection from rock-salt at 22.5° and 67.5°, as in Fig. 4, but reduced to the scale of the present drawing for purposes of comparison. Fig. 4 (a) shows the displaced deposits obtained from the specular beam reflected at 45° from a crystal which was kept at 180°C, when the disks were rotated clockwise and at 450°C when they were rotated counter clockwise. The central undisplaced deposit was obtained by rotating the disks very slowly (about 15 or 20 r.p.m.). Since the outer deposits are the same distance from the undisplaced deposit it is evident that the velocity of the specularly reflected beam does not depend critically upon the temperature of the crystal. It likewise is significant that the form and breadth of the displaced deposits do not differ greatly from that of undisplaced deposit, for the latter, obtained with the disks rotating very slowly, must have just the shape to be expected for a single velocity beam at high speeds of rotation.

The Fraction of the Incident Beam Going into the Specular Beam

To determine what part of the incident beam goes into the specular deposit and what part is diffusely reflected it is necessary to measure the relative intensities of incident and specular beams. This is readily done by weighing the deposits formed when the beams are intercepted by liquid air cooled surfaces. In the apparatus, Fig. 6, a and b are thin pieces of platinum upon which the cadmium was deposited. To eliminate errors due to variation in the rate of emission from the boiler the collecting surfaces were exposed alternately for brief periods. As soon as the apparatus had warmed to room temperature the platinum receivers and deposits were removed, placed in a dessicator, and weighed upon a micro-balance. Repetition of the weighings after two and three days showed that the deposits did not evaporate. Similar deposits on glass evaporate quite appreciably in this length of time.

The receptor a of course receives a portion of the diffusely scattered atoms as well as the specular beam. This diffuse scattering appears to be entirely random and was corrected for on the assumption that this is true. That is, it was assumed that the amount of diffuse scattering into a cone of solid angle $d\omega$ making an angle θ with the normal to the crystal surface was proportional to $d\omega \cos \theta$. In Table I are given the actual weights of specular and direct deposits, and the corrected weight of the specular deposit. From this it

appears that 16 to 17 percent of the incident beam is specularly reflected at 45°.

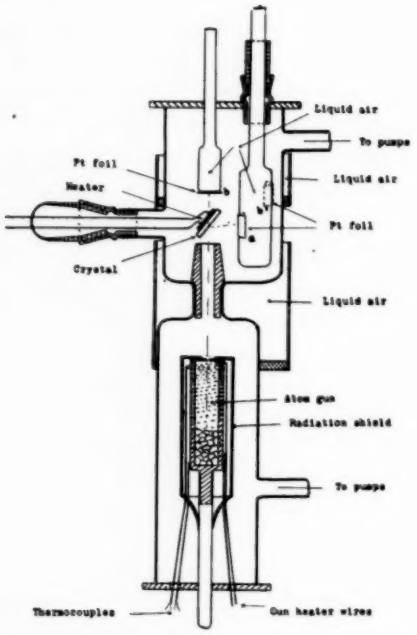

Fig. 6. Type of tube used to obtain quantitative reflection data.

To determine whether the intensity of specular reflection varied with the angle of incidence essentially the same apparatus was used, save that the crystal was mounted to rotate about an axis lying in the plane of the crystal

TABLE I. *Weights of specular and direct deposits. (45°)*

Specularly reflected cadmium Uncorrected	Corrected	Direct beam	Percent specularly reflected
(1) 0.283 mg	0.190	1.060	17.9
(2) 0.197	0.128	0.800	16.0

surface passing through the center of the incident beam. This was done to eliminate the possibility of changes of intensity due to changes in the reflecting surface. Specularly reflected beams were received upon the receptors

TABLE II. *Weights of deposits and corrections for diffuse scattering.*

Angle θ_1	Angle θ_2	Weight of cadmium Uncorrected θ_1	Uncorrected θ_2	Corrected θ_1	Corrected θ_2	Ratio θ_2/θ_1
22.5.	67.5	0.265	0.384	Negligible	0.357	1.35
20.5	66.0	.057	.094	correction	.088	1.54
22.0	66.0	.042	.056		.052	1.24
				Average		1.38

a and b^1, placed on opposite sides of the rotatable liquid air container. This avoided the accumulation of diffusely scattered atoms upon one receptor while the other was being deposited. Variation due to change in rate of emission from the boiler was avoided just as before. Table II gives the weights of deposits and corrections for diffuse scattering.

Discussion

The experiments on reflection from two crystals in succession show that the probability of specular reflection depends upon the velocity and the angle of incidence, for there is evidently a selective action at the first reflection which determines whether the beam when incident upon the second crystal shall be specularly or diffusely reflected. It is not reasonable to suppose that this selection is with respect to anything except velocity. Direct measurements of the reflected velocities confirm this. It is too early to say definitely that the wave-length associated with the translatory motion of an atom is h/mv, as quantum mechanics would have it. Bethe[7] has shown that in the wave picture of the Davisson and Germer experiments there is a quantity analogous to the refractive index in optics, so that the dependence of velocity or wave-length upon the angle of refraction gives an equation

$$\lambda = h/mv = 2d(\mu^2 - \cos^2\theta)^{1/2} \tag{1}$$

for the space grating type of reflection. Here

$$\mu = (1 - \phi/\tfrac{1}{2}mv^2)^{1/2}$$

where ϕ is the average potential energy of the particle when inside the crystal and v its initial velocity. Using this value of μ in Eq. (1) we get

$$\frac{h^2 + 8d^2m\phi}{4d^2m^2v^2} = 1 - \cos^2\theta.$$

So that $1/v^2$ plotted against $\sin^2\theta$ should give a straight line through the origin. So far as our present data go the relation is linear, but the curve does not pass through the origin, see Fig. 7. In fact the data agree within the errors of observation with the equation

$$\lambda' = h/m_H v = 2d(2.26 - \cos^2\theta)^{1/2}$$

Where λ' is the wave-length characteristic of a proton and the refractive index is constant and equal to 1.5 nearly. However it is hard to justify the use of this wave-length[8] and the agreement may be accidental. If the mass of cadmium atom is used we may secure the same agreement by making

[7] Bethe, Naturwiss. **15**, 787 (1927).

[8] Evidence from specific heats (D. M. Dennison Proc. Roy. Soc. **A115**, 483 (1927); Heisenberg, Zeits. f. Physik **41**, 239 (1926)) makes it appear rather certain that protons, like electrons, are governed by the Fermi-Dirac statistics. For alpha-particles however this is probably not the case so that it is not impossible that the wave accompanying the translatory motion of a cadmium atom may have the wave-length which the de Broglie equation would attribute to a helium atom.

$$\mu=(2.26-\phi/\tfrac{1}{2}mv^2)^{1/2}$$

in Eq. (1), and we get a refractive index less than unity.

If diffraction patterns of the plane grating type can be obtained they will serve to fix the wave-length uniquely. With space grating diffraction involving the same power of the velocity on both sides of the equation this

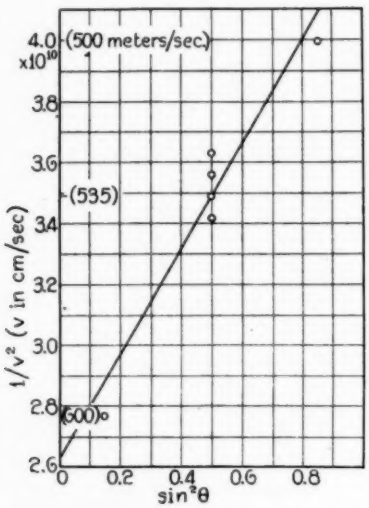

Fig. 7. Experimental curve plotting $\sin^2\theta$ against $1/v^2$.

cannot be done, unless an independent method of measuring ϕ is available. Where the atom reflected is a constitutent of the crystal, ϕ might be computed from heats of formation, and in other cases data on the stability of monomolecular surface layers might yield significant results.

Intensity of Reflected Beams and Resolving Power of Crystals

The intensity of a reflected beam of wave-length λ may be expected to depend upon the number of atoms in the incident beam having wave-lengths between λ and $\lambda+\Delta\lambda$, and upon the resolving power of the crystal. In reflection of x-rays the resolving power $R=\lambda/\Delta\lambda$ will be constant provided the number of crystal planes reflecting is constant. So in the present somewhat analogous situation it may not be unreasonable to suppose that the range of wave-lengths $\Delta\lambda$ over which reflection occurs will vary inversely as λ. The number of atoms in the incident beam having wave-lengths between λ and $\lambda+\Delta\lambda$ is

$$dN=N\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{h^4}{m^4}e^{-\lambda^2/2kTm^2\lambda^2}\frac{1}{\lambda^5}d\lambda.$$

If the probability of reflection drops off regularly decreasing to zero in a range $\Delta\lambda=R/\lambda$ then the ratio of the numbers reflected by crystals set to reflect velocites λ_1 and λ_2 will be

$$\frac{n_1}{n_2}=\left\{\exp\left[-\frac{h^2}{2kTm^2}\left(\frac{1}{\lambda_1^2}-\frac{1}{\lambda_2^2}\right)\right]\right\}\left(\frac{\lambda_2}{\lambda_1}\right)^4.$$

Taking λ_1 and λ_2 to correspond to velocities of 500 to 600 meters per second, the values observed for angles of 22.5 and 67.5°, we find this ratio to be 1.35. The mean of the observed values for angles near these two, given in Table II is 1.38. Obviously in order that 16 percent of the incident beam may be specularly reflected, as at 45° incidence, requires reflection to occur over a considerable range. To form a rough idea of what this range may be it may be well to note that 16 percent of the atoms emerging from the gun have velocities in the range 535 ± 45 meters per second. This represents merely a lower limit, as complete reflection over such a range, dropping at once to zero outside is not to be thought of. On the other hand the range over which appreciable reflection occurs probably does not greatly exceed ±45 meters per second, as otherwise there would be noticeable widening of the deposits obtained with the velocity analyzer. The same conclusion may be drawn from the experiments on reflection from two crystals in succession. When the difference in velocities for the two crystals is as much as 45 meters per second very little specular reflection occurs at the second crystal, most of the beam incident upon it being scattered at random.

A DETERMINATION OF THE STEFAN-BOLTZMANN CONSTANT OF RADIATION

By C. E. Mendenhall
University of Wisconsin, Madison

(Received June 24, 1929)

Abstract

A new method of measuring the constant σ is described in which the radiant energy is measured in terms of electrical input. The results of the study of various possible sources of error are discussed quantitatively. The resulting value of σ is 5.79×10^{-12} watts$\cdot$cm$^{-2}\cdot$deg.$^{-4}$.

THE direct determination of the constant in the Stefan-Boltzmann radiation law, $E=\sigma T^4$, has been the subject of many more or less extended investigations, into a detailed examination of which it is not desirable to enter at present. Suffice it to say that the results range over a large interval, from 5.35 to 6.50×10^{-5} ergs$\cdot$cm$^{-2}\cdot$sec$^{-1}\cdot$deg^{-4}, though there is a considerable "bunching" around a mean about 5.72. The writer has for some time

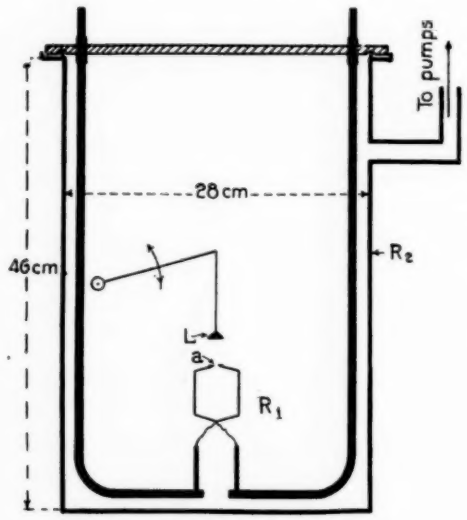

Fig. 1. Diagram of apparatus.

been interested in a method[1] differing from any used by others, which promised possibilities of very considerable accuracy. While these possibilities have not been realized, for reasons which are not at all clear, still various features of the problem have been studied with greater care, I think than ever before. A resumé of the present work therefore seems desirable, even though the conclusions are by no means final. Omitting all details

[1] One form of apparatus involving some of the ideas to be mentioned later, was evolved in conjunction with Dr. C. G. Abbot. Since then, many important details have been changed.

of the evolution of the apparatus, the final form may be described with the aid of Fig. 1, as follows. R_1 is the black body radiator, with electrically heated walls, gold plated on the outside, the temperature of which and the electrical energy input into which can be measured at any moment. R_2 is the receiver, a large brass vessel blackened on the inside, highly exhausted, and immersed either in an ice bath or in a water bath whose temperature is determined. L is a cap or lid, mechanically operated from the outside, which may either rest on the top of R_1 closing the aperture a tightly or may be withdrawn out of the way. The coil wound on R_1 serves at the same time as a resistance thermometer and as a heating element. Thus the temperature of R_1 may be maintained constant (about 100°C) and the electrical input required to maintain this temperature may be measured first with the aperture a shut, and next with the aperture open. The increase in input due to

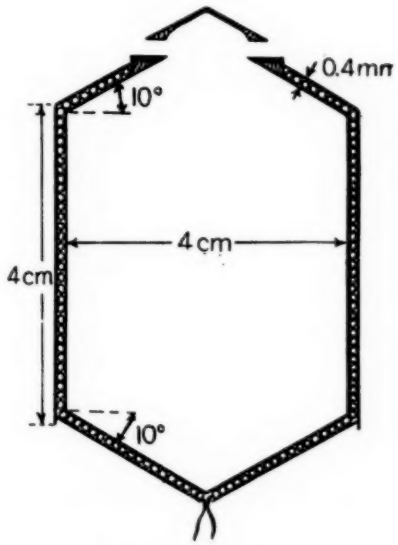

Fig. 2. Detail of radiator.

opening the aperture measures the major part of the black body emission from the radiator, but to this must be added a relatively small correction (about 5 percent) due to the emissivity of the gold lid when it covers the aperture. In order to discuss the possible errors of the various measured quantities it will be necessary to describe parts of the apparatus in greater detail.

The radiator. This is made of copper in three parts (Fig. 2). The inner, with walls 0.07 to 0.1 mm thick, is coated with platinum black on the inside and, except for the circular aperture and the gold rim around it, has its outer surface entirely covered by a coil of No. 40 silk-enamel nickel wire wound non-inductively with the two ends at the center of the closed end of the radiator. The coil is soaked in shellac and baked in place tightly attached to the copper walls. The outer surface of the wire then receives a thin coat of shellac, and an outer copper sheath, having the same wall

thickness but gold plated on the outside, is carefully fitted over the coil and baked into place. That part of the inner vessel in which the aperture is cut is made of solid gold. The result is a light, rigid structure, polished gold over its entire outer surface, platinum blacked over its inner surface, having a circular aperture carefully beveled on the inside, while the outer surface for a few millimeters around the aperture is ground and polished to a fair degree of optical flatness. Nickel wire was chosen for the coil because of its specially constant resistance and large resistance temperature coefficient. Careful annealing before insulating gave it quite permanent characteristics, and it made a reliable resistance thermometer as well as a uniformly distributed heating element. The outer surface of the radiator was made of polished gold with the obvious intention of reducing the external radiation losses as much as possible, and the radiator was supported by quartz rods only, for the same reason. It is not necessary to know the exact nature of these losses, since they do not enter into the final result. Suffice it to say that the black body emission through the aperture was about one-third of the total input when the lid was shut. In order to vary the conditions, two sizes of radiators were used, and two sizes of receivers but the exact dimensions are unimportant. The dimensions given in Fig. 2 are for the larger radiators and receiver. Various sizes of aperture were also used, as will be discussed later.

The lid. The lids were at first made of gold plated copper, and later of solid gold because the emissivity of polished solid gold could be reproduced with great accuracy, and better contact with the radiator was also secured. They had a somewhat heavier rim which was ground and polished flat to make good contact with the corresponding rim on the radiator. The inner surface of the lids was blackened. They were hung by a silk fibre passing through a central hole about 0.1 mm in diameter.

The receiver and bath. It is unnecessary to consider details of these. Essentially the receivers were brass vessels, blackened on the inside with lamp black mixed with very dilute shellac, connected to a pumping system and liquid air trap so that pressures of 10^{-6} mm Hg or less could be maintained in them, to reduce external conduction loss from the radiator and possible absorption difficulties. The baths were vigorously stirred, and a constant temperature was maintained either by continually supplying ice or by a thermostat when working near room temperature.

The equation for σ is

$$\sigma=\frac{(i_0^2-i_s^2)R+\sigma_G A_L(T_L^4-T_1^4)+H_c-\sigma_G A_2(T_2^4-T_1^4)}{a(T_2^4-T_1^4)}$$

where i_0 = equilibrium current, aperture open, in amperes; i_s = equilibrium current, aperture shut, in amperes; R = resistance of radiator coil at T_2°C in ohms; a = area of aperture; A_L = area of exposed surface of lid; A_2 = area of gold rim of radiator covered by lid; H_c = conduction loss by thermocouple when used to operate lid; T_1 = temperature of receiver; T_2 = temperature of radiator; T_L = temperature of lid; σ_G = emissivity of gold.

Attention should be called to the fact that the low emissivity of the external gold surface and the lid had two advantages—first, the radiation through the aperture was relatively large, from 1/3 to 1/2 of the total losses with the aperture closed; and second, the terms depending on σ_G in the above equation are only 4 to 5 percent of σ, so that σ_G itself need not be known to a very high degree of accuracy. The determination of the quantities entering into the equation for σ will next be considered.

Measurement of resistance of coil. Coil resistances were measured by a 10:1 Wheatstone bridge built up of standard resistances in oil and a standard Wolff box. Compensating leads were provided, and the bridge was frequently tested by substituting a known resistance in place of the radiator coils.

Current measurements. The current in the radiator coils was measured with a Tinsley potentiometer, by measuring the voltage drop over a standard 10 ohm coil inserted in the bridge in series with the radiator. A standard 100 ohm coil in the opposite arm served to compensate for this. Standard cells with B. S. certificates were used. The accuracy of reading was far beyond that necessary.

Temperature measurements. The radiator temperature T_2 was sometimes placed between 99° and 100°C, and sometimes around 110°C, chosen because the first could be obtained in a hypsometer using water, and the second in one using toluene. The toluene was redistilled and its boiling point determined as a function of barometeric pressure by comparison with some carefully calibrated platinum thermometers of Dr. Roebuck's. In every case the radiator was used at a temperature lying directly in the calibrated range, so that no extrapolation was necessary. While the resistance of the radiator coils showed a slow change with time, this was so gradual that the calibrations always repeated themselves in a very satisfactory manner, indicating a very small error in the determination of the radiator temperature by using its heating coil as a resistance thermometer. The current used in calibrating was relatively so small that its heating effect was negligible. The *sensitivity* of the coil as a resistance thermometer was ample, one millimeter deflection on the bridge galvanometer corresponding to about 0.001°C. The temperature of the receiver was determined by the use of mercury thermometers which were calibrated at the ice-point directly and for the range near room temperature by comparison with a thermometer calibrated at the Bureau of Standards. These thermometers could be read to 0.05°C, and the calibration was good to 0.1°C or less.

Determination of gold emissivity. It was first intended to determine σ_G each time from the total area of the closed radiator and the energy input required to maintain equilibrium. Such a determination is, however, subject to errors due first to almost unavoidable crevices where the two parts of the outer shell join, to temperature differences due to variable contact between outer shell and coil, and somewhat to variations in the emissivity of the gold plated on copper. We therefore began to use pure gold lids, and determined σ_G by making flat recessed disks of solid gold, about 3 cm diameter and 1.5 mm thick, made in two parts with a silk enamel nickel coil stuck

with shellac between the two parts, all cracks being carefully closed and burnished over. This method gave very consistent results for σ_G, the two best values being 2.396 and 2.372×10^{-13} watts $\cdot$ cm$^{-2} \cdot$ deg^{-4}. This concordance is quite sufficient, for the reason already given. In order further to vary conditions, one radiator and lid were platinum plated. In this case, the emissivity of the lid was determined from the total emissivity of the closed radiator.

The measurement of the aperture. The apertures used ranged from about 7 mm to 15 mm in diameter, the edge being extremely sharp and formed by the intersection of an internal conical and an external flat surface, the latter being ground and polished. The angle included between the two surfaces was about 13°. Measurements were made with a Gaertner travelling microscope along several diameters of each aperture. Readings were made to 0.001 mm and the micrometer screw was corrected by comparison with a standard meter (B. S. certificate). Several observers carried out the measurements and the agreement was very satisfactory. Had there been any marked tendency to measure systematically too large or too small, one would expect it to show up as a systematic dependence of the final results upon the size of the aperture—but no such dependence was apparent.

Summing up, the temperature of the radiator coils was certainly determined to within ± 0.03°C, the resistance to better than 1 part in 5000, and the currents measured to 1 part in 10,000. All this looks very promising—but it was early discovered that while any one radiator would give very consistent results, even with different temperature limits, and after repeated recalibrations, various radiators gave results which spread in a surprising and discouraging way. Our time has been spent on a study of the various sources of error which might enter into the present method and which might account for the differences between radiators. Since we have studied these with more care than has been usual, and since most of them enter in one way or another into every method used for determining σ, our conclusions have some general interest, even though our final results are as yet by no means as consistent as had been hoped for.

Possible Sources of Error

1. *Radiators* not "perfect"—i.e., not black bodies. If E is the emissive power and R the reflecting power of our black body *aperture*, then $E = 1 - R$, and also $R = R_s \int e' ds + R_s^2 \int e'' ds + \cdots$ where R_s is the intrinsic reflecting power of *inner* surface, e' is the percentage of any radiation striking an element of the inner surface which, reflected once according to Lambert's Law, escapes through the aperture, and e'' the corresponding percentages escaping after two reflections. Since R_s can be made quite small the second and higher terms are practically negligible. In practice, the integration was replaced by a summation, and this was carried out graphically by dividing the interior surface into symmetrical zones. In our case the area of the aperture varied from 0.8 to 2 percent of the entire inner surface, and the value of the coefficient of R_s above, which might be called the "geometric reflecting power,"

was found to be 0.011 for the particular case where the "aperture ratio" was 1.7 percent. For smaller proportional apertures the "geometric reflecting" power would be still smaller.[2] It follows that even with R_s as high as 10 percent $R=0.0011$ plus negligible higher order terms, and $E=0.9989$, which for present purposes may be considered perfect. Actually it was probably better than that, since the reflecting power of electrolytic platinum black as recorded is much less than 10 percent.

2. *Receiver not perfectly absorbing.* Calculations similar to the above gave $R=R_s\times 4\times 10^{-4}$. In this case R_s was probably larger (lamp black), but even assuming $R_s=20$ percent, the effective absorbing power would be $A=1-R=1-(0.8\times 10^{-4})=0.999+$

3. *Temperature drop from coil to inner radiating surface.* (a) *From coil through insulation to copper walls.* An idea of the probable magnitude of this was obtained by using two silk insulated copper coils shellaced on opposite faces of a copper disk in the same way that the radiator coils were mounted on the inner part of the radiator. One of these was electrically heated to about 100°C, the other unheated, and each was used as a resistance thermometer. The results showed that to maintain the actual heat flow occurring in the radiator required a temperature drop of only 0.004°C, which is quite negligible.

(b). *Drop through the layer of platinum black.* This is very difficult to determine, and the only experimental evidence we have is approximate and will be given under the next heading. However, the fact that the ratio of aperture to internal area was always small favored a small drop through the platinum black since the amount of energy transmitted through each square centimeter of platimum black was correspondingly small.

4. *Non-uniform temperature of inner wall.* That even the thin inner copper walls of the radiator would have a large effect in wiping out temperature differences was demonstrated by winding two coils on a copper cylinder the same size, shape, and thickness (0.1 mm) as the inner shell of the radiators, each coil occupying half the length. One being electrically heated to 100°C and the other unheated and used as a thermometer, it was found that the unheated coil had a mean temperature of 99°. Since the difference is so small in this extreme case, it would appear that the effects of small irregularities of heating would be fairly well smoothed over by the conductivity of the inner copper shell. Even if the contact of the coil with the inner shell were bad over half the area, it would hardly seem possible that this could produce as great a non-uniformity in temperature as was observed under the extreme conditions of the above test when there was no heating at all over half the area.

A further examination of the internal wall temperature was made under the usual vacuum conditions by soldering a small gold disk to the junction of a very fine calibrated iron-constantan thermocouple (0.02 mm diameter)

[2] For a spherical radiator with an opening in one side the computation may be carried out by simple integration, and it follows that $R=R_s$ (area of opening/2 area of sphere)+higher order terms.

and lowering the couple through the black body aperture until the disk rested on the lower end wall of the radiator. Observations of this sort were made on three different radiators, two of which showed a wall temperature 0.1° lower than the coil, and the other less than 0.3° lower. It is possible though not probable that the gold disk (3 mm diameter) served as a shield to the surface it covered, and hence indicated a temperature slightly too high; but at all events, it is clear that there were no *large* temperature differences involved. If the temperature of the inner radiating surface were slightly lower than that of the coil, the effect would be to make the observed σ too small. On the other hand, since we determined the *mean* temperature of the coil, if the inside wall temperature followed this *mean*, but varied from point to point, the effect would always be to give too *high* a value of σ. However, a simple computation shows that even if half the wall were as much as 5° high and half 5° low, the effect on the observed σ would be to raise it by only 0.2 percent.

5. *Poor contact of coil with outer sheath.* The primary danger from this source is in the non-uniform inner temperature which might result, but from the observations referred to under "4" it does not seem likely that the inner temperature could be very much disturbed. Nevertheless, there were undoubtedly much greater variations in the contact with the outer sheath than with the inner shell, and this item remains one of some uncertainty. An attempt was made to study the temperature distribution on the outer walls by touching them at various points with the junction of an extremely fine thermocouple. For this the radiator had to be in air, and hence conditions necessarily were rather unsteady, but no difference could be found greater than 3°, and much of this may have been due to varying convection.

6. *Temperature of the lid.* Conductivity and internal radiation would keep the lid at a temperature somewhat near that of the radiator, but to get a more accurate knowledge of its condition the temperatures of two lids were determined under working conditions by replacing the silk fibre usually used to lift the lids on and off by the fine thermocouple referred to above. Correction was made for the lowering of the lid temperature due to the conduction of heat by the couple. The results agreed in indicating a lid temperature very closely 10° below that of the radiator, and such a temperature was used in computing this small correction.

7. *Cracks between lid and rim on which it rested.* The grinding and polishing of these surfaces has been referred to above, and there were never any cracks present which could be observed with a magnifying glass. The uniform results obtained with different gold lids on any one radiator are further evidence that "cracks" were largely eliminated. Even if there were a gap 0.03 mm wide around the entire circumference of the lid, it would only introduce an error of about 1 percent in σ.

8. *Radiation through hole in lid.* This was entirely negligible, since the area of the holes was only about 0.01 percent of the aperture.

9. *Imperfect equilibrium.* Since it required eighteen or twenty minutes for the radiators to reach equilibrium after closing the lid and eight minutes

after opening the lid, one might question the accuracy with which the equilibrium point could be determined. However, a plot of the heating currents at constant temperature, against time, while equilibrium was being established showed that there was no cause to worry about this.

10. *Incomplete closing of the aperture due to lid coming down eccentrically.* The centering of the lid was controlled by sensitive levels, which occasionally got out of adjustment. As a rule, incomplete closing was evidenced by irregularity of results. In a few cases, it was found that a particle of dust lodged under the lid and prevented proper closing.

11. *Errors in determining the temperature of radiator or receiver.* A simple computation shows that an error of 0.1° in the radiator temperature T_2 would result in an error of less than 0.2 percent in σ, while the same error in T_1 would produce an error of less then 0.1 percent in σ. Such errors might be of either sign. As indicated above the determination of T_2 appears to be reliable to 0.03°C, and that of T_1 to 0.1°C. It seems perfectly certain that accidental errors in temperature measurements cannot be of any significance compared to other factors and that a *systematic* error in σ greater than 0.2 percent due to temperature errors is large as one would expect.

12. *Possible effect of high vacuum on resistance of coil.* In general, the resistance of the radiator coils as a function of temperature was determined in air at atmospheric pressure, whereas the coils were used in a high vacuum. In order to ascertain whether the reduced pressure altered the coil resistance, the hypsometer was fitted with a vacuum vessel so that a calibration could be carried out at a pressure less than 0.001 mm. While this was not as low as the operating pressure, it was certainly low enough to indicate whether any such pressure effect were present. The calibration in vacuum agreed within the limits of measurement with that carried out at atmospheric pressure.

13. *Change in temperature distribution from "open" to "shut" condition.* It is obvious that the distribution of temperature across the substance of the heating coil will be different for the "open" and "shut" conditions of the radiator. When the radiator is shut the inside surface of the wires will be at the highest temperature, the gradient across the wire being sufficient to carry off the heat generated in the wire and lost from the outside surface. When the radiator is "open" the temperature will be highest at some point in the wire, with a gradient toward outside and inside, determined respectively by the heat loss on the outside and on the inside of the radiator (through the aperture). Since the ordinary procedure involves keeping the *mean* temperature of the wire the same for both "open" and "shut" readings, this change in temperature distribution across the heating wire will in general involve a slight *rise* in temperature of the outer surface of the wire, and therefore a slight increase in the heat lost from the outer surface of the radiator. Such an increase in external loss would result in the measured value of σ being too large, and it is necessary to compute the magnitude of this error. As a first approximation we considered a conducting plane of nickel, of a thickness equal to the diameter of the wire, and assumed that heat was being generated

in this sheet at the same rate per unit volume as in the actual wire. The open condition would correspond in this case to the carrying of Q calories per sec per cm^2 away from one side of the sheet and $3Q$ calories per sec per cm^2 from the other side, this being about the ratio of energy loss through the aperture to external loss in the actual case. The "shut" condition would correspond to zero loss of heat from one side and a loss of $3Q$ calories per sec per cm^2 from the other. A computation based on these considerations and involving the dimensions, currents, and resistance of the radiator coils, shows that the surface temperatures of the nickel sheet would change by less than 0.0001°C due to the change from the "shut" to the "open" conditions of heat flow. Since this change in the idealized case is much too small to concern us, the conclusion seems justified that even in our actual case the outer surface of the wire, and therefore the outer surface of the radiator, did not change in temperature by an appreciable amount in passing from the "open" to the "shut" condition.

Consideration of these sources of error shows that numbers 1, 2, 3, 6, 7, 8, and 10 could only result in making the observed σ too small. On the other hand, certain combinations of good and poor contacts (4 and 5 above) between the coil and the inner and outer sheaths would make the observed σ too large, because of the resulting non-uniform temperature of the inner wall, but to produce any considerable error in σ would require, as has been pointed out above, considerable difference of temperature from point to point, and no direct evidence of such large differences has ever been found.

Results

Some ten radiators have been constructed in the attempt to run down systematic sources of error and the cause of variations between radiators. Of these, three gave results (using gold plated lids) which differed from the mean of all by as much as ± 10 percent. In case of one of these giving a very high value of σ we removed the outer shell and put on a new coil and outer sheath, and after reconstruction the radiator gave a value of σ near the mean of all. This indicates that the abnormal value was not due to anything connected with the aperture, or with the inner blackening, since these were not altered during reconstruction. As already mentioned, no entirely satisfactory explanation of these large variations in the behavior of different radiators has been found. All the possible causes of which we have thought have been studied (1 to 13 above) and the only ones which seem at all adequate are certain combinations of poor contact of the coil with the internal and external copper elements of the radiator. We found, however, that the three radiators giving the most widely divergent values of σ showed a change of their characteristics with time. Two other radiators also had variable time characteristics. Now, a change with time is certainly an indication of something wrong, so we have eliminated from final consideration all those radiators which showed such a change. There remain five radiators which have shown consistent behavior over long periods during which they have been in and out of the vacuum chamber many times, their resistance-temperature

calibration remaining essentially constant. Two of these have also been used for a number of sets of observations with solid gold lids. In computing the results obtained with gold plated copper lids we have assumed that these lids had essentially the emissivity of solid gold. We have therefore used in these computations the value of gold emissivity determined with the solid gold disks as previously described. The temperature of the lids was determined by comparison with that directly measured with solid gold lids, and in all cases the temperature (T_2) of the internal radiating surface was taken to be that of the coil. In order to show the degree of consistency obtainable with a given radiator, Table I gives the results obtained with radiator No. 9, with three different solid gold lids. As before stated, these observations were taken at intervals over a considerable time.

TABLE I. *Results with radiator No. 9 and different solid gold lids.*

Lid No. 1	Lid No. 2		Lid No. 3	
5.80	5.82	5.80	5.76	5.76
5.80	5.80	5.79	5.76	5.76
5.82	5.79	5.79	5.77	5.76
	5.80	5.80	5.76	

Table II is a summary of the final results, these being averages for each of the radiators which showed stable characteristics.

TABLE II. *Summary of final results.*

Designation	Aperture / Inside Area	$\sigma \times 10^{12}$ (watts · cm^{-2} · deg^{-4})	Temp. range (°C)
	Gold plated lids		
No. 6 small	0.016	5.91	0–99
No. 8 small	0.017	5.80	0–99 22–99
No. 7 small	0.022	5.72	0–99 24–99
No. 9 large	0.016	5.75	0–99.2 21–99.2 24–99 24–109.5
No. 3 large	0.017	5.74	0–99.2
	Average	5.78	
	Solid gold lids		
No. 9 large	0.016	5.79	25–99
No. 3 large	0.017	5.80	26–99
	Platinum lid and radiator		
No. 4 large	0.0175	5.63	0–99

The results with the gold plated lids are subject to some uncertainty in the value of the lid emissivity, and also the lid temperature. They are nevertheless given, for since they involve five different radiators and different values of T_1 and T_2, their mean tends to eliminate systematic characteristics of individual radiators and certain temperature ranges. The result obtained with the platinum plated radiator must be given less weight than the others for two reasons: the emissivity of the platinum plated lid was not directly determined, and the measured change in input produced by opening and closing is relatively less because of the larger emissivity of platinum. The results with solid gold lids, since they depend on directly measured lid temperatures and the measured emissivity of solid gold, would appear to deserve the greatest weight, and the value

$$\sigma = 5.79 \times 10^{-12} \text{ watts} \cdot \text{cm}^{-2} \cdot \text{deg}^{-4}$$

is therefore the best mean for all the results.

In view of the fact discussed above, that most of the residual errors which are difficult to evaluate operate to reduce the observed value of σ, the results certainly suggest that the commonly accepted value (5.709×10^{-12} watts $\cdot$ $\text{cm}^{-2} \cdot \text{deg}^{-4}$, Int. Crit. Tables) is somewhat too low. It is interesting to notice that certain of the more recent determinations of σ point in the same direction. Hoffmann[3] obtained a value of 5.76_4 and Kussmann[4] a value 5.79_5 in exact agreement with that of the present work.

I am glad to acknowledge particular indebtedness to Mr. T. B. Godfrey and Mr. J. H. Dillon who have assisted in this work.

[3] Hoffman, Zeits. f. Physik **14**, 301 (1923).
[4] Kussmann, Zeits. f. Physik **24**, 58 (1924).

SURFACE TENSION OF MERCURY IN THE PRESENCE OF GAS UNDER VARYING PRESSURES

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Abstract

Quincke's method with Worthington's correction was used. Contrary to the accepted values the maximum surface tension of mercury (515 ± 7 dynes/cm at 31°C) is reached when only mercury vapor is present. A surface freshly created in a gas at 760 mm has a high initial tension approaching that when the surface is created in mercury vapor. The tension falls as the gas is adsorbed until an equilibrium value for a given pressure is attained. As the pressure is reduced the equilibrium value rises to a maximum which depends upon the nature of the gas. For instance, this maximum tension for mercury-hydrogen occurs at the critical pressure of 2.8 mm. If the pressure is lowered to stiction the tension remains unchanged so long as the mercury is not agitated beyond a certain amount. This maximum value for mercury-hydrogen is 441 dynes/cm which is less than the mercury-mercury vapor value of 515 dynes/cm. If the mercury-hydrogen is violently agitated when the pressure has been reduced to stiction the tension approaches 515 dynes/cm, the mercury-mercury vapor tension. Vibrating drop methods tend to give the vacuum value of the surface tension even when a gas is present at atmospheric pressure.

I. Introduction

ACCORDING to Professor Jauncey of Washington University it has been found that the surface tension of a mercury surface produced in a vacuum (i.e. except for the mercury vapor above the liquid mercury) is greater than the tension of a mercury surface produced in a gas such as air. However, if the surface is first produced in a vacuum and then a gas is admitted the tension does not immediately become that of a mercury surface produced in the gas. On the other hand, Freundlich[1] in his book on "Colloid and Capillary Chemistry" quotes J. Stoeckle[2] as stating that the value of the tension of mercury in a vacuum is less than the initial value of the tension of mercury surfaces created in the presence of gases. Thus there seems to be two distinct experimental findings in regard to the tension of mercury in the presence of gases. Since the experiments quoted by Freundlich were done before 1900 and since vacuum technique has been much improved since then, it seems worth while to investigate this matter anew and hence this present research.

II. Description of Apparatus and Experimental Methods

The apparatus as first used was designed and built by Dr. F. E. Poindexter, who had previously used a similar device in investigating the surface tension of melted metallic sodium.[3] Slight changes have been made as the

[1] H. Freundlich, Colloid and Capillary Chemistry (translated by H. S. Hatfield), p. 82.
[2] J. Stoeckle, Wied. Ann. **66**, 499 (1898).
[3] F. E. Poindexter, Phys. Rev. **27**, 820 (1926).

experiments progressed. A glass cup *A*, Fig. 1, forms the top of the glass tube *B*, which tube passes through the wall of the cup chamber *C* to which it is hermetically sealed. The upper edge of *A* is ground true and smooth with emery and the inner edge lapped so as to present a truly circular rim free from chipped places caused from grinding the top edge. A plate glass window *D*, with its center at the level of the top of the drop and vertical in position is sealed to the side of the cup chamber as shown. The cup chamber extends a considerable distance below the cup *A* forming a catch-well for mercury spilled from *A* so that the cup may be refilled without disturbing the apparatus. The tube *B* extends upward outside the cup chamber and reenters it at *F*. This tube has a constriction at *G* as shown, the purpose of which will be explained later. Into the vertical part of the tube *B* the tube *H* is sealed. This tube *H* is inclined upward, the higher end leading to the vacuum pumps.

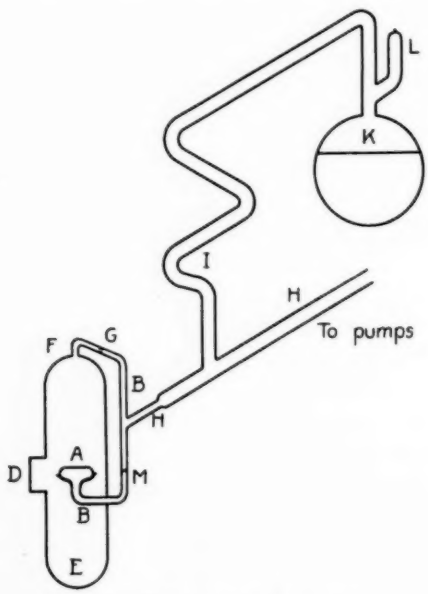

Fig. 1. Diagram of apparatus.

Extending upward from *H* is a condenser tube *I*, coiled for compactness, leading from the flask *K* of 250 cm³ capacity. A filling tube *L* enters the flask. This tube is sealed off after filling the flask with mercury. This apparatus as well as the mercury vapor pump and the McLeod gauge are entirely of Pyrex glass all fused together into one piece.

Each unit of the apparatus before assembling was cleaned in boiling chromic acid, washed with distilled water and dried with heated and filtered air. The mercury was aerated for several hours by drawing air through it by means of an aspirator. It was then treated successively with caustic soda, nitric acid, chromic acid and distilled water. It was then distilled and redistilled directly into the flask *K* through the tube *L* which was at once sealed off. The whole apparatus was then thoroughly out-gassed by exhaustion

while a blast flame was played over the entire apparatus including the mercury vapor pump and McLeod gauge. This out-gassing process was repeated frequently during the progress of the experiments.

When it is desired to examine a drop of mercury for its surface tension the apparatus is either exhausted or filled with any gas in the presence of which it is desired to generate the mercury surface to be examined. Heat is then applied to the flask K and mercury distilled over. This condenses in the condenser I, runs down through H into B, then upward into the cup A filling it from the bottom and producing a new surface as the mercury fills the cup and stands above its edge due to its surface tension. In order that there may still be no possibility of this surface being contaminated from contact with the glass it is customary to distill over an excess of mercury allowing it to spill into the well E thus assuring a perfectly fresh and uncontaminated surface on the mercury in the cup.

The drop in A is viewed through the telescope of a cathetometer. Beside the telescope is placed a lamp with a horizontal slit in front of it. This slit

Fig. 2. Mercury drop with background.

is on the same level as the axis of the telescope. When the axis of the telescope, the slit and the point on the curved surface of the drop at which a tangent plane to the drop is vertical are all in the same plane, a bright star is observed at the cross wires of the telescope.

The exact location of the top of the drop is much more difficult. A clean mercury surface is a practically perfect, first-surface mirror, especially when viewed, as in this case, tangentially. For this reason it perfectly reflects any back-ground that can be placed behind it and so, at the extreme top, perfectly blends with the background making the top of the mercury indistinguishable from the background. To overcome this difficulty a background ruled with alternate black and white lines was made and this was placed behind the mercury with the lines inclined at about 30° from the vertical. the angle formed between the parts of the lines visible above the mercury and their reflection is sharply marked as shown on the accompanying Fig. 2, and it was found that the location of the surface of the mercury can be read in the cathetometer within an accuracy of 0.01 mm and these readings can be consistently repeated.

When it is desired to clean all the mercury out of the cup so as to have entirely fresh mercury in the cup all that is necessary is to exhaust the apparatus to a fairly good vacuum and then let in air, or any other gas, rather rapidly. The constriction G prevents the gas from flowing freely into the chamber C through the top, thus producing considerable pressure on the mercury at M, blowing the mercury out of the cup.

III. Calculation of the Surface Tension

Quincke's[4] formula as corrected by Worthington[5] was used. With the approximations suggested by Worthington the formula for the tension, T, is

$$T/\rho = h^2g/2 + (2hTg)/\rho(1/b - 1/3.282L) \tag{1}$$

where ρ is the density of mercury, h is the difference between the equatorial line at the position where the mercury surface is vertical and the top of the drop, L is the radius of the equatorial circle and b is the radius of curvature at the top of the drop and g is the acceleration of gravity. Since in the present experiments $L = 2.4$ cm, we may discard the term containing b so that

$$T = \frac{h^2\rho g}{2(1+2h/3.282L)}. \tag{2}$$

These experiments were done in August with a temperature of 31°C, at which temperature the density of mercury[6] is 13.519 gm/cm³. In St. Louis $g = 980.0$ and the formula becomes

$$T = 6624h^2/(1+0.2538h) \tag{3}$$

As the vernier of the cathetometer reads directly to 0.02 mm and under the microscope can be estimated to 0.01 mm an error of 0.01 mm on each reading is assumed. Since each determination of h requires a reading both of the star and of the top the error in the value of h is twice this amount or ± 0.02 mm which at $h = 2.82$ mm gives an error in surface tension of ± 6.8 dynes/cm.

IV. Surface Tension in a Vacuum

After filling the flask K, Fig. 1, with mercury and sealing off L so that the whole apparatus, including the mercury-vapor pump, is one piece of hermetically sealed Pyrex glass, the pumps were started and when a high vacuum was reached a blast flame was applied to the whole apparatus so as to out-gas it thoroughly as described above. After the apparatus had cooled the vacuum was maintained at "stiction" and mercury distilled over till the cup was filled and overflowed.

Contrary to the results obtained by J. Stoeckle and G. Meyer,[7] the maximum surface tension was found to be that of mercury in a vacuum, i.e.,

[4] G. Quincke, Phil. Mag. **41**, 245 (1871).
[5] A. M. Worthington, Phil. Mag. **24**, 51 (1885).
[6] International Critical Tables **2**, 458.
[7] G. Meyer, Wied. Ann. **66**, 523 (1898).

mercury-mercury vapor, a value as high as 515 dynes/cm being obtained. It must be remembered, however, that this result is obtained only when all the conditions are at the limit of their perfection. The above is the maximum surface tension obtained during the whole course of these experiments. The measurements were very carefully checked. If less care is taken in outgassing a lower value of the tension is obtained.

V. Surface Tension in Various Gases

In order to obtain consistent results when the mercury was in contact with gases it was found to be very necessary to keep the surface free from vibration and extension. If a fresh mercury surface is generated in contact with a gas the tension is at first high approaching the value in a vacuum. The tension soon falls, as first noticed by Quincke,[8] till it reaches equilibrium with the gas at the existing pressure. If now the surface of the mercury be agitated beyond a certain amount, either by the addition of more mercury from below thereby stretching the surface, or by spilling some thereby rupturing the surface, there will occur an instantaneous rise in the surface tension, the extent of such rise in tension depending upon the kind of gas to

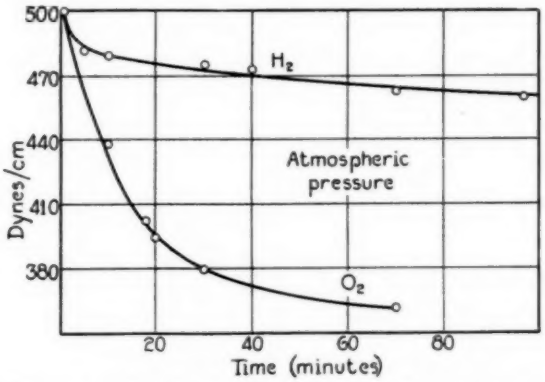

Fig. 3. Variation of surface tension with time from exposure to gas.

which the mercury is exposed and upon the amount of disturbance. This rise in tension is accompanied by the liberation of gas from the mercury in quantities measurable on the McLeod gauge as pointed out by Stoeckle who attributed it to a gas film condensed on the mercury surface. In one case the tension of mercury in contact with hydrogen at a pressure of 0.00015 mm remained constant at 421 dynes/cm over a period of 8 minutes. On spilling a drop from the mercury, however, the tension immediately rose to 473 dynes/cm and remained constant at this value for 14 minutes. Simultaneously the pressure of the hydrogen rose to 0.00048 mm.

After exhausting and thoroughly outgassing the apparatus, purified gas of the desired kind is admitted up to atmospheric pressure. Mercury is then distilled over into the cup *A* till it overflows, thus creating a fresh mercury

[8] G. Quincke, Pogg. Ann. **105**, 1 (1858).

surface in the presence of the gas. The distillation is then stopped and the surface tension observed as it lowers, approaching equilibrium. The curves of Fig. 3 show how the tension decreases with the time after a fresh surface has been produced in contact with hydrogen or oxygen at atmospheric pressure. During these observations great care was taken to keep the apparatus free from any mechanical disturbance.

The curves of Fig. 4 show the effect of exhausting the gas after the mercury has been standing in contact with the gas at atmospheric pressure for two or three hours. In these curves the readings at the various pressures were taken at intervals of time shorter than the time necessary for the equilibrium tension to be established at each pressure. For this reason no points are shown. The curves merely show the general trend. It will be noticed that reducing the pressure of the hydrogen had no effect on the surface tension till about 10 mm was reached when the tension suddenly began to rise. A similar effect is noticed in the case of CO_2 but the curve has a

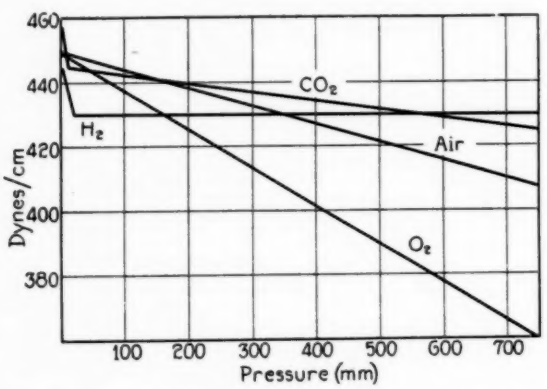

Fig. 4. Variation of surface tension as gas pressure is lowered.

considerable slope before reaching its critical pressure of about 6 mm. The tension when oxygen and air are the gases, on the other hand, begins to increase as soon as exhaustion begins so that if they have a critical pressure of this nature it is greater than 760 mm.

On decreasing the pressure below the critical pressures for the respective gases, the tension rises until a second critical pressure occurs below which no further rise in the tension occurs even when the pressure is lowered to stiction and kept at stiction for several hours. These first and second critical pressures together with the corresponding tensions are shown in Table I.

It must be remembered that the apparatus must be kept free from mechanical vibration in order to obtain these critical pressures. The final tension obtained is decidedly lower than that of a mercury surface produced in a vacuum.

Next, the apparatus was thoroughly exhausted and outgassed. While the vacuum is maintained mercury is distilled over from *K*, Fig. 1, into *A* till it piles up and runs over, thus creating a fresh mercury surface in a vacuum.

When the apparatus has assumed room temperature carefully purified gas of the desired kind is then admitted, either slowly or rapidly as required and the mercury in A observed through the cathetometer as described above, great care being taken to keep the apparatus free from vibration. The initial

TABLE I. *Critical pressures for mercury in various gases.*

Gas	First critical pressure (mm)	First critical tension (dynes/cm)	Second critical pressure (mm)	Second critical tension (dynes/cm)
Hydrogen	10	430	2.8	441
Carbon dioxide	6	445	3.5	455
Air	—	—	1.0	451
Oxygen	—	—	1.0	451

surface tension before admitting the gas was, as mentioned in section IV under the most favorable circumstances, about 515 dynes/cm but it could easily be brought to 491 dynes/cm with reasonable care. There was never observed the slightest tendency of the surface tension of the mercury to increase, even temporarily, upon admission of hydrogen, dry air, carbon dioxide, or oxygen whether the gas was admitted very slowly or rapidly enough to bring the pressure up to 760 mm in one minute. On the contrary, there set in at once, upon admission of the gas, a decline of surface tension

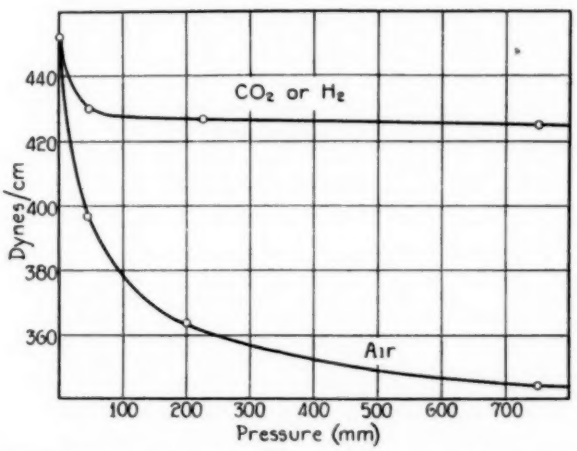

Fig. 5. Variation of equilibrium surface tension with gas pressure.

which varied in rapidity with the kind of gas used. Final equilibrium is reached only after long periods of time and is dependent upon the pressure and nature of the gas. At almost any pressure above stiction and below the second critical pressures of Table I, the tension finally comes to the values given in the last column of this table. At pressures below the second critical pressure for a gas the surface tension decreases from the vacuum value as the time from the instant of admission of the gas increases. The decrease of tension is accompanied by a decrease in the pressure of gas. As an example

the tension in hydrogen decreased from 495 dynes/cm to 484 dynes/cm in 20 minutes while the pressure decreased from 0.0037 mm to 0.0020 mm.

At pressures greater than the critical pressures, the equilibrium values of the tension for various pressures of carbon dioxide, hydrogen and air are shown in Fig. 5. Each point shown was obtained after allowing at least 13 hours for the tension to come to equilibrium at the pressure indicated. Because of these long intervals only few points are shown.

VI. Discussion

Contrary to the findings of Stoeckle the surface tension of mercury is found to be higher when the surface is produced in a vacuum than when the surface is produced in the presence of a gas. The explanation of Stoeckle's results is that even minute traces of gas lower the tension by about 50 dynes/cm below the true vacuum value. Further the vacuum value of 515 dynes/cm which was obtained in these experiments can only be obtained when a fresh surface is created in a vacuum made as perfect as possible by outgassing. The lowest pressure obtained by Stoeckle was 0.0004 mm and this is much too great to be considered as a vacuum. Further it has been found that if mercury has been in contact with a gas and then the gas exhausted the tension will not rise above about 455 dynes/cm no matter how low the pressure is made unless the surface is subjected to mechanical disturbance. If the surface is disturbed violently enough the tension will rise suddenly. Because of this fact, vibrating drop methods of measuring surface tension tend to give a value approaching that of a surface produced in a vacuum even though the vibrating drops are in the presence of a gas.

In conclusion the writer desires to thank Professor G. E. M. Jauncey for suggesting this research and Professor Ward of the Department of Chemistry for much valuable discussion regarding this problem.

SOUND PROPAGATION IN GAS MIXTURES

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(Received May 13, 1929)

Abstract

An earlier treatment of the propagation of sound in mixtures of two gases is generalized and simplified somewhat. The essential point of the theory is the consideration of the internal energy variations by the assignment of fictitious internal state temperatures which, in the simplest case assumed here, are taken to be constant for each of the component gases. The long wave-length velocity expression is directly interpretable as a Laplace formula for a gas of mean reciprocal mass and averaged specific heat. From a more general point of view the velocity of propagation of infinitesimal waves is always given by the Laplace result provided a frequency variation of specific heats be recognized. Explicit mention is made of the detailed effect of viscosity and the two conductivities. Experimental data support theory.

IN A recent paper,[1] the writer presented a theory of the propagation of sound in a single gas and mixtures of two gases. The present article extends the results on mixtures to the case of n gases and provides simpler forms for some of the earlier formulae. It also comments from a kinetic standpoint on the roles of viscosity and translational and internal energy conductivities.

The point of view taken is that the internal energy fluctuations of the various types of molecules are not of the same amount or synchronous in phase with the translational energy variations. We suppose however that each gas W may be characterized by a parameter ω_W such that if the translational temperature variation in a given region be δT the changes in the number of molecules in the various energy levels correspond to a temperature change $\omega_W \delta T$. The assumption that ω_W is independent of the quantum state considered, is, of course, a strong restriction. (An assumption tantamount to it for one gas has been used by Herzfeld and Rice[2] in their important work on sound propagation in a pure gas.) The very general analysis in I for the case of a single gas shows that some arbitrary postulate regarding the dependence of ω_W on the internal state considered is essential in order to make headway. It would seem worthwhile to investigate the consequences of various other functional relations between internal state r and ω_{W_r}.

The symbols to be used exclusive of those whose connotations seem sufficiently obvious are: M = number of distinct gases comprising the mixture. m_W = mass of molecule of gas W. N_W = number of type W molecules. N_{W_r} = number of type W molecules in the quantum state r. $S/N = \Sigma N_W / N m_W$ = mean value of the reciprocal molecular mass of the mixture. β_W = half the

[1] D. G. Bourgin, Phil. Mag. Vol. 7, 821, (1929). This paper will be referred to as I.
[2] K. F. Herzfeld and F. O. Rice, Phys. Rev. 31, 691 (1928).

number of normal coordinates[3] in the internal energy of a type W molecule. $N_W N_R L_{WR}$ = energy increment in gas W/ unit time due to collisions of W and R type molecules, for unit energy difference $(3k/2)$ between translational and internal energy of the gas W molecules[4]. $\phi_W = \sum^M N_W N_R L_{WR}$. K_W = kinetic energy of a type W molecule. The equipartition principle indicates $K_W \underset{W}{\equiv} K$. $\dot{x} = dx/dK$. $\nu = 2\pi n$, where n is the frequency.

The equations for this work[5] are written for a one dimensional problem (i.e., an infinite plane source)

$$\frac{\partial}{\partial t} N_W = -\frac{\partial}{\partial x} N_W v \tag{1.1}$$

$$\frac{\partial}{\partial t} Nv = -\frac{\partial}{\partial x} \frac{2}{3} S\,K + \frac{4}{3} \mu \frac{S}{N} \frac{\partial^2 v}{\partial x^2} \tag{1.2}$$

$$\frac{\partial}{\partial t} NK = -\frac{\partial}{\partial x} \frac{5}{3} NKv + \Delta K + \psi \frac{\partial^2 K}{\partial x^2} \tag{1.3}$$

$$\frac{\partial}{\partial t} N_{W_r} = -\frac{\partial}{\partial x} N_{W_r} v + \Delta N_{W_r} + \gamma_{W_r} N_W \frac{\partial^2}{\partial x^2} N_{W_r}/N_W \tag{1.4}$$

μ is the coefficient of viscosity. The last terms in Eqs. (1.3) and (1.4) are the heat conduction terms and it will be observed that because of the use of K instead of T, ψ is $2k/3$ times the value of the usual conduction coefficient. The presence of the coefficients of conduction and viscosity outside the double differentiation is justified by the order of the approximations we shall make. For the same reason terms representing the interdiffusion effect and the dissipation[6] function have been omitted from Eq. (1.3). It is, of course, clear that μ, ψ and γ_{W_r}[7] are functions of $N_1, \cdots, N_M$.

Since double and higher frequency terms are to be neglected we may assume that the variables vary sinusoidally about equilibrium values and that coefficients of products of harmonic functions are vanishingly small. The amplitudes of the harmonic terms are distinguished by the customary variation symbol δ as prefix. It can be shown, Cf. I, that the collision increments may be written

$$\Delta K = \delta K \sum^M \phi_W(\omega_W - 1) \tag{2.1}$$

$$\Delta N_{W_r} = \delta K(1-\omega_W)\ \dot{N}_{W_r} \sum^M C_{W\hat{R}}\, N_R. \tag{2.2}$$

[3] This definition is preferable to the one involving the ambiguous term degrees of freedom used in I.

[4] Cf. I, Eq. (28), for the expression in terms of transition probabilities.

[5] Cf. I for the most important terms in these equations.

[6] Lamb, Hydrodynamics, p. 518.

[7] That γ_{W_r} is of the nature of a heat conductivity coefficient for the internal energies is immediately obvious on multiplying Eq. (1.4) by ϵ_r and summing over r and W. We should then get the internal energy change equation. The ratio N_{W_r}/N_W occurs with the differentiating operator because this term is obviously to be independent of change in concentration alone.

Another useful relation is

$$\delta N_{Wr} = N_{Wr}\frac{\delta N}{N} + \omega_W \dot{N}_{Wr}\delta K .$$

The solution for ω_W is

$$\omega_W = \frac{\dot{N}_{Wr}\sum C_{WR}N_R}{j\nu\dot{N}_{Wr} + \dot{N}_{Wr}\sum C_{WR}N_R + \gamma_{WrWr}\dot{N}\nu^2/V^2} . \tag{3.1}$$

An argument given in I leads to

$$C_{WR} = 3L_{WR}/2\beta_W .$$

Hence

$$\omega_W = 1 - j\nu\frac{2}{3}\frac{\beta_W}{\sum N_R L_{WR}} - \frac{4}{9}\frac{\nu^2\beta_W{}^2}{(\sum N_R L_{WR})^2} - \frac{2}{3}\nu^2\frac{\gamma_{Wr}}{V_0{}^2} + j\nu^3\left[\partial_W{}^3 + \frac{\partial_W{}^2\gamma_W}{V_0{}^2} + \frac{\partial_W\gamma_W d_1}{V_0{}^2}\right] \tag{3.2}$$

where

$$\partial_W = 1/\sum C_{WR}N_R$$

$$\frac{1}{V^2} = \frac{1}{V_0{}^2}\cdot 1 - j\nu d_1 \cdots d_1 > 0$$

It is to be remembered that the internal energy change* is $\int_{T_0}^{T}(1-\omega_W)\phi_W\delta K dT$ and is to be compared with the translational energy increment detailed by the terms exclusive of ΔK in Eq. (1.3). In both cases the lowest order term is the one in ν. Accordingly the† *in phase* increase of internal energy depends for its rate on the specific heat and finite transition time; the lag, or ν^2 term, on internal conduction besides. Viscosity and external conduction appear in d_1 (Cf. Eq. (3.2)) to modify the relative amplitude of internal energy changes in the next higher term.

The fiction of an internal temperature may be waived and instead one may employ a variable specific heat $B(\nu)$ determined either from the fact that the internal energy increases by an amount $B_W(\nu)k\delta T$ for a change δT or that the rate of variation in internal energy is $\nu B(\nu)k\delta T\cos\nu t$. There result the two equivalent definitions

$$B_W(\nu) = \omega_W B_W(0) \left(= \tfrac{2}{3}\omega_W\beta_W\right)$$

$$= (1-\omega_W)\sum{}^{M} N_R L_{WR} \tag{4}$$

After some not very difficult eliminations of the amplitude terms in Eqs. (1.1) $\cdots$ (1.4) we may write the key equation

* It may be pointed out that if ω_W is to be independent of r to the second order in ν, it is necessary to drop the subscript r from γ_{Wr}.

† I contains a minor error of statement as regards this point.

$$V^2=\frac{SK}{3N}\,\frac{\frac{10}{3}Nj\nu+2\sum(1-\omega_W)\phi_W+\frac{2\psi\nu^2}{V^2}+j\frac{4\mu\nu}{KN}N}{Nj\nu+\sum(1-\omega_W)\phi_W+\frac{\phi\nu^2}{V^2}} \tag{5}$$

where

$$N=N_j\nu+\sum(1-\omega_W)\,\phi_W+\frac{\psi\nu^2}{V^2}$$

From Eq. (5) the low frequency velocity is approximately

$$V_0^2=\frac{SK}{3N}\,\frac{\frac{10}{3}N+\frac{4}{3}\sum N_W\beta_W}{N+\frac{2}{3}\sum N_W\beta_W}\,. \tag{5.1}$$

The first order approximation for V_0, as contrasted with the absorption term, is practically independent of the assumptions made about the dependence of ω_W, on r (Cf. I). To the next approximation

$$V=V_0\left[1+j\nu\frac{2}{3}\left(\frac{\frac{4}{9}N\sum^M\frac{N_W\beta_W{}^2}{\sum^M N_R L_{WR}}+\frac{N}{V_0{}^2}\left\{\psi+\frac{2}{3}\sum\gamma_W N_W\beta_W\right\}}{\left(N+\frac{2}{3}\sum N_W\beta_W\right)\left(\frac{10}{3}N+\frac{4}{3}\sum N_W\beta_W\right)}+\frac{\mu S}{N^2V_0{}^2}\right)+\cdots\right] \tag{5.2}$$

The interpretation of the remarkably simple result for the long wavelength velocity is that the mixture behaves like a single gas of averaged specific heat and averaged reciprocal mass* and that Eq. (5.1) is the Laplace value for the velocity in this hypothetical single gas[8] (clearly the ratio in Eq. (5.1) is proportional to the effective specific heats at constant pressure and constant volume).

It is instructive to make a further step and to look upon Eq. (5.2) as a Laplace formula still, with specific heats, functions of the frequency. More explicitly the translational specific heat at constant volume ($3k/2$) is affected to the next order by the translational conductivity while the numerator which refers to constant pressure involves, due to the relative motions implied in expansion and contraction, the viscosity term as well. Similarly the internal specific heat $\beta(\nu)$ which has already been explicitly characterized (Cf. Eq. (4)) depends on transition times and internal conductivity and to a still higher order on viscosity and translational conductivity.

This point of view makes the study of sound propagation more intuitive. It is, then, only necsesary to know how the internal and trans-

* Not as has sometimes been supposed the averaged mass (Cf. H. Benndorf, Phys. Zeits. **4**, 97 (1929)).

[8] The form of the analogous expression (which is now seen to be reducible) appearing in I obscured this direct generalization of the Laplace formula and the above interpretation was given there for the case $L_{WR}\underset{R}{\equiv}L_W$, only.

lational energies change at constant volume and constant pressure respectively. Inclusion of new terms or modifications of the theory can start directly with the extended Laplace formula and the real meaning of the changes seen immediately without necessity of recourse to the original differential equations.

Chapman[9] has given the value of ψ and μ for a mixture of monatomic gases. From the form of his results it seems that to a first approximation in the general case the coefficients would involve the ratio of quadratic forms in the concentrations at the least.[10] Even for the comparatively simpler problem assumed by Chapman a theoretical computation would be most awkward—hence for a test of Eq. (5.2) it would be necessary to obtain μ, γ_W and ψ experimentally as functions of the concentrations of the gases.

The absorption term[11] depends on the ratio of a cubic to a biquadratic in the concentrations (not including the change in V_0).[12] The extreme assumption $L_W \equiv \underset{R}{L_W}$ would allow us to treat the mixture as a single gas of averaged β^2/L so that experiments on the component gases might be used to predict that part of the absorption due to the finite time required for internal energy transitions. This should be a fair working assumption for gases of similar natures.

One of the first tests of a theory of sound in mixtures ought to be the derivation of the velocity of sound in air. Clearly since β is the same for O_2 and N_2 we have

$$\frac{V_{12}}{V_2}=\frac{1}{m_{12}}\Big/\frac{1}{m_1}=\frac{1}{5}\,\frac{4m_2+m_1}{m_1m_2}\Big/\frac{1}{m_1} \tag{6}$$

1, 2 and 12 refer to N_2, O_2 and air respectively.

Lechner's[13] value 315.5m/sec for V_2 leads to $V_{12}\sim 332.5\ m$/sec which is in very close agreement with Pierce's result 331.94 m/sec.

For application of Eq. (5.1) to a case where the gases are of different heat capacities we shall consider the influence of water vapor in air. It is readily substantiated that

[9] Chapman, Phil. Trans. **98**, 252 (1915).

[10] The occurrence of ψ in higher order terms is due to its associated factor $1/V^2$ (Cf. Eq. (5)). The presence of γ_W is only partially due to an analogous cause (Cf. Eq. (3.2)). Hence although both conductivity coefficients enter the phase lag expression in a parallel way and may in fact be conveniently reduced to the single effective coefficient $\psi+(2/3)\sum N_W\beta_W\gamma_W$ the next and higher order approximations show asymmetry in their action.

[11] The form given is somewhat more perspicuous than the special expression occurring in I which is reducible Cf. note 9.

[12] Our theory has been illustrated for an infinite vibrating plane—a case which may not correspond to the experimental practice studied. For effects due to motion in two or three dimensions, slight modifications (amounting in general to symmetrizing the expressions as regards x, y, and z) are to be made in Eqs. (1.1) to (1.4). Then, retaining the harmonic form of the time factor, the space coordinate dependence may be obtained by solving the equations under the limitations of small variations and the appropriate initial and boundary conditions. In a very general case, besides the causes taken account of in our treatment, attenuation may be due to wave spreading, lateral and radial diffusion, vorticity, change of wave form, wall reactions, double frequency effects, etc.

[13] Lechner, Wiener Ber. **11**, 1035 (1909).

$$\frac{\delta V}{V}=\frac{N_2}{2N}\left[\frac{m_1-m_2}{m_2}-\frac{8(\beta_2-\beta_1)}{(4\beta_1+10)(2\beta_1+3)}\right] \tag{7}$$

where N_2/N is the moisture ratio of air, m_1 is the m_{12} defined in Eq. (6) and the subscripts 1, 2 refer to air and water vapor respectively. Substitution of the appropriate values leads to $\delta V/V \sim 0.006+$ for *N.T.P.* Recent[14] unpublished experimental work by Professor Pierce's students suggests a variation of almost 0.005. The two figures are satisfactorily close.

The writer is further informed by Professor Pierce that the latest work in his laboratory does not support a frequency dependence of the velocity in air.[15] This is in complete accord with theoretical prediction since the values of the dissipation terms in the case of air are very small. The previous positive results were due to the fact that the apparent measured velocity varies with distance from the source. This latter anomalous effect is probably a matter of experimental method rather than a characteristic of the physical situation though the energy dissipation progressively increases the wavelength very slightly. It may be that corrections for the displacement of the node from the boundary of the vibrating source or consideration of the sphericity of the waves forming the stationary wave pattern may account for the result but it is perhaps unprofitable to speculate in the absence of details.

[14] Earlier negative results (Proc. Am. Ac. Arts and Sci. **60**, 271 (1925)), are explained as due to a hitherto unsuspected effect. Cf. the concluding remarks of this paper.

[15] A curve of the type published by Pierce for air, i.e., involving maxima or minima could be formally accounted for by a large fourth order effect of opposite sign to the second order term. In any particular case, however, the parameters involved could all be estimated from the low frequency velocity and absorption and independent data and hence the permissibility of the explanation tested. It is clear too that neglected terms in our equations would affect the higher approximations. Cf. also Note 12. In this connection it may be remarked that a falling velocity-frequency characteristic is not impossible, for Eq. (5) yields for the ν^2 velocity correction the following negative sum, besides the usually predominant positive terms

$$\frac{\nu^2}{V_0^2}\left\{\frac{\psi+\frac{2}{3}\Sigma\beta_W\gamma_W}{V_0^2}+\frac{4}{9}\sum\frac{N_W\beta_W^2}{\Sigma N_R L_{WR}}\right\}^2\Bigg/\left\{1+\tfrac{2}{3}\textstyle\sum N_W\beta_W/N\right\}$$

Comparison with the positive terms involving the conductivities indicates that in general their effect is in the direction of decreasing velocity (Compare Herzfeld-Rice, reference 2).

THE JOULE-THOMSON EFFECT AND HEAT CAPACITY AT CONSTANT PRESSURE FOR AIR.

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Abstract

The constants for air in the equation of state of Beattie and Bridgeman are evaluated from the p-v-T data of Holborn and Schultze, and this numerical equation is used to compute μC_p at various temperatures and densities. From the C_p data at one atmosphere of the Reichsanstalt for air, corresponding values of C_p at the same temperatures and densities are calculated by means of the equation of state. The values of μ obtained from these two sets of calculations are plotted along isotherms against the corresponding pressures and the values at even pressures and various temperatures are in good agreement with the experimental data of Roebuck. The computed C_p data are compared with those of Roebuck and of Holborn and Jakob and are in good agreement with the values obtained by these experimenters. The Joule-Thomson inversion curve obtained from the equation of state is in good agreement with the experimental values given by Roebuck.

ALL the thermodynamic properties of a substance may be evaluated over a given range of variables, if pressure-volume-temperature data are available and if any thermal property is known as a function of temperature over the range concerned. The evaluation in general can be effected most conveniently by means of an equation of state which represents the pressure-volume-temperature data. For accuracy, it is necessary that the equation of state reproduce all the pressure and volume trends with temperature as well as the actual pressures. If an equation satisfying these requirements is available, it is possible to calculate all the thermodynamic properties of a substance with an accuracy comparable to that obtained by direct experimentation, and hence such values serve a useful purpose in cases where data have not been obtained directly or where the field has only been partially covered.

Recently J. A. Beattie and the author[2] have formulated an equation of state which reproduces the data on 10 gases to 0.1–0.2 percent, and which gives derivatives of considerable accuracy. This equation is of the form

$$p=\frac{RT(1-\epsilon)}{v^2}[v+B]-\frac{A}{v^2} \qquad (1)$$

where $B=B_0(1-b/v)$; $A=A_0(1-a/v)$ and $\epsilon=c/vT^3$. The existence of good p–v–T data and C_p data at one atmosphere for air has made it possible to

* Contribution No. 204.

[1] National Research Fellow in Chemistry.

[2] Beattie and Bridgeman, J. Am. Chem. Soc. **49**, 1665 (1927); ibid, **50**, 3133 (1928); ibid, **50**, 3151 (1928); Proc. Am. Acad. Arts. Sci. **63**, 229 (1928).

compute the Joule-Thomson coefficients and C_p at various temperatures and pressures, and thereby test the equation of state by comparing the computed values with those determined experimentally.

The most recent, accurate p–v–T data on air have been published by Holborn and Schultze[3] who covered the range from 0° to 200°C up to pressures of approximately 100 atmospheres. The constants in the equation of state (1) were evaluated from these data using the method previously outlined.[2] The constants are as follows:[4]

$$R=0.08206 \qquad c=\ 0.12\times10^{6}$$
$$B_0=0.04070 \qquad b=-0.02174$$
$$A_0=1.0763 \qquad a=\ 0.01697$$
$$T=t+273.13$$

in units of liters per mole, atmospheres and absolute Centigrade degrees. A comparison of the observed and calculated values, expressed in the original units, is given in Table I. The agreement is very good, the average deviation in pv over the whole field being 0.0002 or 0.014 percent.

TABLE I. *Comparison of observed pv products with values computed from the equation of state. Pressures in meters of mercury; temperatures in °C; pv products in Reichsanstalt units referred to pv=1.0000 at 0°C and 1 meter of mercury.*

Pressure		Values of pv 200°	150°	100°	50°	0°
10	obs.	1.7406	1.5555	1.3695	1.1825	0.9934
	o-c	−0.0002	0.0001	0.0001	0.0001	−0.0001
20	obs.	1.7484	1.5612	1.3726	1.1818	0.9870
	o-c	0.0000	0.0002	0.0002	0.0002	−0.0001
30	obs.	1.7565	1.5674	1.3762	1.1818	1.9817
	o-c	0.0000	0.0002	0.0002	0.0002	0.0000
40	obs.	1.7650	1.5740	1.3805	1.1826	0.9774
	o-c	0.0000	0.0002	0.0003	0.0001	0.0000
50	obs.	1.7739	1.5811	1.3854	1.1841	0.9742
	o-c	0.0001	0.0001	0.0003	−0.0001	0.0001
60	obs.	1.7831	1.5887	1.3909	1.1864	0.9720
	o-c	0.0000	0.0001	0.0003	−0.0003	0.0002
70	obs.	1.7927	1.5967	1.3970	1.1804	0.9709
	o-c	0.0001	0.0001	0.0004	−0.0006	0.0003
80	obs.	1.8027	1.6052	1.4037	1.1932	0.9708
	o-c	0.0002	0.0001	0.0005	−0.0007	0.0004

Total average deviation = 0.0002

[3] Holborn and Schultze, Ann. d. Physik **47**, 1089 (1915); see also Holborn and Otto, Zeits. f. Physik **10**, 367 (1922); ibid, **23**, 77 (1924); ibid, **33**, 1 (1925).

[4] These constants are somewhat different from the values obtained by correlating all the p-v-T data on air in the literature (see ref. 2). The present data were employed since they are the most recent and are the only set of values which cover the temperature range used by Roebuck in his Joule-Thomson work.

For the evaluation of μC_p in terms of the equation of state, it is convenient to write equation (1) in the form

$$p=\psi T-\phi-\Gamma/T^2 \tag{2}$$

where

$$\psi=\frac{R}{v^2}[v+B]\ ;\quad \phi=\frac{A}{v^2}\quad \text{and}\quad \Gamma=\frac{\psi_c}{v}$$

and hence all three are functions of volume only. Differentiating (2) with respect to temperature at constant pressure, there results

$$\left(\frac{\partial v}{\partial T}\right)_p=\frac{\psi+2\Gamma/T^3}{\psi' T-\phi'-\Gamma'/T^2}$$

where ψ', ϕ', and Γ' are the first derivatives with respect to volume. The usual expression for the Joule-Thomson effect then becomes

$$\mu C_p=T\left(\frac{\partial v}{\partial T}\right)_p-v=\frac{\psi T+2\Gamma/T^2}{\psi' T-\phi'-\Gamma'/T^2}-v. \tag{3}$$

By substitution of the respective volume functions and rearrangement, equation (3) reduces at zero pressure to the following

$$\mu C_{p_0}=\frac{2A_0}{RT}-B_0+\frac{4c}{T^3}\,. \tag{4}$$

In equations (2) and (3), v and T are the independent variables and hence values of μC_p were calculated for a number of constant densities at various temperatures from 0° to 280°C. These densities were evenly spaced (every mole per liter) and the number used on each isotherm was such as to correspond to a pressure range from 0 to about 250 atmospheres. The values at zero pressure were obtained from equation (4). The use of p and T as the variables would be very laborious since along any isobar there would be a different value of the volume functions in equation (3) at each temperature.

To obtain the values of μ from μC_p, it is necessary to have the corresponding values for C_p. The heat capacity of air at a pressure of one atmosphere has been measured at the Reichsanstalt[5] over a considerable range of temperature and can be represented by the following formula:

$$C_p=0.2405+0.000019t.$$

The computation of C_p directly at higher pressures fom the one atmosphere values requires the use of the second derivative of volume with respect to temperature at constant pressure and the integration of a complicated function of v and T at constant temperature from 1 to p atmospheres. This function is too involved for convenient manipulation and so ΔC_v and C_p-C_v

[5] Scheel and Heuse, Ann. d. Physik **37,** 79 (1912); ibid, **40,** 492 (1913); Heuse, Ann. d. Physik **59,** 86 (1919); Holborn and Austin, Wissensch. Abh. **4,** 131 (1905); Holborn and Henning, Ann. d. Physik **18,** 739 (1905); ibid, **23,** 810 (1907).

were used, both of which are comparatively simple functions of v and T. As given by the equation of state, these relations are

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v = -\frac{6\Gamma}{T^3}$$

$$\Delta C_v = C_v - C_{v0} = -\frac{6}{T^3}\int_\infty^v \Gamma dv$$

$$= \frac{6Rc}{v^2T^3}\left[v + \frac{1}{2}B_0 - \frac{1}{3}\frac{bB_0}{v}\right] \tag{5}$$

$$C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_v = -\frac{T(\psi + 2\Gamma/T^3)^2}{\psi' T - \phi' - \Gamma'/T^2}$$

$$= (\mu C_p + v)(\psi + 2\Gamma/T^3) \tag{6}$$

$$C_p = C_{v0} + \Delta C_v + [C_p - C_v]. \tag{7}$$

The C_p values of the Reichsanstalt at one atmosphere were changed to C_v values at zero pressure using equations (5) and (6) and these can be accurately represented by the following relation over the temperature range from 0° to 300° in 15° calories per gram.

$$C_{v_0} = 0.1714 + 2.3\times10^{-5}t - 1.0\times10^{-8}t^2 \quad (0° - 300°\text{C}).$$

A series of values of ΔC_v and $C_p - C_v$ were computed by (5) and (6) corresponding to the densities and temperatures used for μC_p and were added to

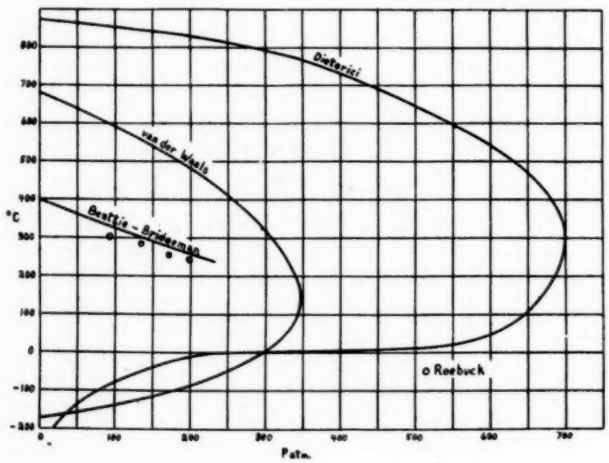

Fig. 1.

the C_{v0} values to give C_p according to relation (7). These C_p data were then divided into the corresponding values of μC_p thereby giving μ in terms of density and temperature as the variables.

The transformation of variables from density $(1/v)$ to pressure was effected by plotting μ along isotherms against the pressures corresponding to these even densities, which were calculated by means of the equation of state. From this plot, the values of μ were read off at even pressures. A comparison of these calculated values with those obtained experimentally by Roebuck[6] is given in Table II, the pressures and temperatures being those used in his paper. The agreement is satisfactory with the exception of the 0° isotherm, and the part of the 25° isotherm at higher pressures. Examination of the original data of Roebuck indicates that his values of μ are considerably more uncertain in this portion of the field. On the other isotherms, the agreement is essentially the same at high as at low pressures, notwithstanding that the constants of the equation of state were deduced from data extending only to 100 atm. and the pressure range of Table II is a little more than twice that amount.

TABLE II. *Comparison of computed values of μ with the experimental values of Roebuck.* $\mu \times 10^3$ (°C/atm.)

Press. (atm.)		0°	25°	50°	75°	100°	150°	200°	250°	280°
1	obs.	266	227	189	158	133	93	63	40	30
	calc.	274	227	189	159	134	95	66	43	32
	o-c	−8	0	0	−1	−1	−2	−3	−3	−2
20	obs.	249	212	178	149	124	86	56	35	25
	calc.	259	213	177	148	124	87	59	38	28
	o-c	−10	−1	1	1	0	−1	−3	−3	−3
60	obs.	214	182	153	128	106	71	45	25	16
	calc.	225	185	152	126	105	71	47	28	19
	o-c	−11	−3	−1	2	1	0	−2	−3	−3
100	obs.	178	152	128	107	89	59	35	16	8
	calc.	190	156	128	106	87	58	36	19	11
	o-c	−12	−4	0	1	2	1	−1	−3	−3
140	obs.	145	124	105	88	72	47	26	9	1
	calc.	157	129	106	87	71	46	26	11	4
	o-c	−12	−5	−1	1	1	1	0	−2	−3
180	obs.	113	97	83	70	58	37	19	3	−5
	calc.	129	106	87	71	57	35	18	4	−2
	o-c	−16	−9	−4	−1	1	2	1	−1	−3
220	obs.	81	72	63	54	45	29	13	−2	−11
	calc.	106	88	71	58	46	26	11	−2	−8
	o-c	−25	−16	−8	−4	−1	3	2	0	−3

In Table III (a) the calculated values of μ at 1 atm. and at 0°, 50° and 100° are compared with those given by Roebuck,[6] Joule and Thomson,[7] Noell[8] and Hoxton,[9] while in Table III (b) a comparison is made with data

[6] Roebuck, Proc. Am. Acad. Arts Sci. **60**, 537 (1925).

[7] Joule and Thomson, Scientific Papers (Joule), **11**, p. 16. Collected Papers (Thomson), **1**, p. 333.

[8] Noell, Selbstverlag d. Verein. Deut. Ing., No. 184, Julius Springer, Berlin, 1916.

[9] Hoxton, Phys. Rev. (2), **13**, 438 (1919).

computed from the measurements of Bradley and Hale[10] by Keyes.[11] The agreement between the results of Bradley and Hale and those calculated at 0° by the author adds confirmation to the opinion that the data of Roebuck are in error at this temperature.[12]

TABLE III (a). *Comparison of observed and computed values of μ at 1 atmsophere pressure.*

Temp.	Joule-Thomson	Noell	Hoxton	Roebuck	Computed
0°C	0.275	0.278	0.303	0.266	0.274
50°	0.204	0.185	0.226	0.189	0.189
100°	0.147	0.125	0.170	0.133	0.134

TABLE III (b). *Comparison of observed and computed values of μ at 0°C.*

Pressure	Bradley & Hale	Computed
50 atm.	0.233	0.234
100	0.192	0.190
150	0.152	0.149
200	0.117	0.117

Porter[13] has pointed out that the Joule-Thomson inversion curve, conditioned by $\mu = 0$, is a very sensitive test of an equation of state. Points on this curve have been computed by means of the equation of state (1) and the agreement with the experimental inversion points obtained by Roebuck is shown in the figure, where for comparison curves calculated by means of the equations of van der Waals and Dieterici are also included. These latter curves were taken from Roebuck's paper. Considering the accuracy with which Joule-Thomson or p–v–T measurements must be made in order to obtain accurate inversion points either experimentally or by computation, the agreement of the Beattie-Bridgeman curve with the data of Roebuck is satisfactory.

The computed values of C_p based on the one atmosphere data of the Reichsanstalt and the equation of state were transformed from units of liter-atmospheres per mole into 15° calories per gram (one 15° calorie per gram equals 1.1960 liter-atmospheres per mole, where the molecular weight of air is taken as 28.960).[14] These values were plotted against the corresponding pressures in a similar manner to that employed for μ. Values were read off at even pressures and are compared with the data of Roebuck in Table IV. The agreement is good, being about 1 percent over practically the entire field, the main deviations occurring at low temperatures and high pressures similarly to those found for μ. Since the data of Roebuck are obtained from his measurements of the Joule-Thomson coefficients, this is to be expected.

[10] Bradley and Hale, Phys. Rev. (1), **29**, 258 (1909).

[11] Keyes, J. Am. Chem. Soc. **43**, 1452 (1921).

[12] At 150 atm. the value of 0.1515 is used instead of 0.1615 as given by Keyes, since the former lies on a smooth curve through the other points, and apparently is the correct value.

[13] Porter, Phil. Mag. (VI) **11**, 554 (1906).

[14] Beattie and Bridgeman, J. Am. Chem. Soc. **50**, 3151 (1928).

TABLE IV. *Comparison of computed values of C_p with the experimental values of Roebuck. C_p in 15° calories per gram.*

Press. (atm.)		0°	25°	50°	75°	100°	150°	200°	250°	280°
20	obs.	0.249	0.249	0.248	0.248	0.247	0.247	0.246	0.247	0.247
	calc.	0.250	0.249	0.248	0.247	0.247	0.246	0.247	0.247	0.247
	o-c	−0.001	0.000	0.000	0.001	0.000	0.001	−0.001	0.000	0.000
60	obs.	0.266	0.263	0.260	0.258	0.256	0.253	0.251	0.250	0.249
	calc.	0.274	0.266	0.260	0.257	0.255	0.252	0.251	0.250	0.250
	o-c	−0.008	−0.003	0.000	0.001	0.001	0.001	0.000	0.000	−0.001
100	obs.	0.280	0.276	0.272	0.268	0.265	0.260	0.257	0.254	0.252
	calc.	0.298	0.283	0.273	0.267	0.263	0.258	0.255	0.254	0.253
	o-c	−0.018	−0.007	−0.001	0.001	0.002	0.002	0.002	0.000	−0.001
140	obs.		0.287	0.282	0.277	0.273	0.266	0.261	0.257	0.254
	calc.		0.299	0.285	0.276	0.270	0.263	0.259	0.257	0.256
	o-c		−0.012	−0.003	0.001	0.003	0.003	0.002	0.000	−0.002
180	obs.		0.296	0.290	0.284	0.279	0.271	0.264	0.260	0.257
	calc.		0.314	0.296	0.285	0.277	0.268	0.262	0.259	0.258
	o-c		−0.018	−0.006	−0.001	0.002	0.003	0.002	0.001	−0.001
220	obs.		0.302	0.296	0.289	0.284	0.275	0.268	0.262	0.259
	calc.		0.327	0.306	0.292	0.283	0.272	0.265	0.262	0.260
	o-c		−0.025	−0.010	−0.003	0.001	0.003	0.003	0.000	−0.001

In Table V a comparison is made with the data of a number of investigators[15] at 59° and various pressures. The data of Holborn and Jakob[16] are

TABLE V. *Comparison of observed and computed values of C_p at 59°C.*

Press kg/cm²	Holborn & Jakob	Joule & Thomson	Vogel	Noell	Roebuck	Computed
25	0.2490	0.2481	0.2480	0.2493	0.2493	0.2485
50	0.2554	0.2557	0.2543	0.2568	0.2563	0.2557
100	0.2690	0.2721	0.2664	0.2701	0.2699	0.2697
150	0.2821	0.2919	0.2770	0.2812	0.2813	0.2827
200	0.2925	0.3150	0.2853	0.2893	0.2901	0.2942

expressed as the mean heat capacity between 20° and 100°C which is taken by Partington and Schilling as equivalent to 59°. The data of Roebuck are calculated from those at 60° as given in his paper. Very good agreement is obtained with the values of Holborn and Jakob and of Roebuck.

[15] The data of Joule and Thomson, Vogel and Noell are taken from Partington and Schilling, The Specific Heat of Gases, Van Nostrand, New York, 1924, p. 161.

[16] Holborn and Jakob, Forschungsarbeiten d. Verein. Deut. Ing., 187 and 188, 1916. Holborn, Scheel and Henning, Wärmetabellen der Physikalisch-Technischen Reichsanstalt, Friedr. Vieweg & Sohn, Braunschweig, 1919.

ADDITIONAL SERIES LINES IN THE SPECTRA OF C II AND N II

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(Received July 5, 1929)

Abstract

Several of the strong lines of C II have been identified as combinations of the ^4P term of the sp^3 configuration with the quartet terms observed by Fowler and Selwyn. This fixes the term values $^4P_1=206810.7$, $^4P_2=206789.2$, $^4P_3=206760.6$. In N II, the term value of the ^1S term of the s^3p^3 configuration, has been fixed at 206159, and of the ^1P term of the sp^3 configuration at 72084 relative to the term values given by Fowler and Freeman. The ^1S term combines with the ^1D term of the same configuration to give the nebular line at 5754.8A. A large number of terms including those which Fowler and Freeman designated by "a" have been shown to belong to the quintet system. These have the following relative term values: sp^3s, $^5P_1=90000$, $^5P_2=89943.8$, $^5P_3=89873.1$; $sp^3\cdot p$, $^5S=65759.0$, $^5P_1=69994.5$, $^5P_2=69970.7$, $^5P_3=69926.9$, $^5D_0=71955.0$, $^5D_1=71939.8$, $^5D_2=71909.6$, $^5D_3=71866.5$, $^5D_4=71812.6$; $sp^2\cdot d$, $^5D_1=50658.5$, $^5D_2=50650.6$, $^5D_3=50639.3$ $^5D_4=50624.9$, $^5F_2=52611.4$, $^5F_3=52585.3$, $^5F_4=52551.6$, $^5F_5=52511.1$; sp^3, $^5S=248812(?)$.

Spectra of C II

IN THEIR recent analysis of the C II spectrum, Fowler and Selwyn[1] have fixed all of the important doublet terms and most of the high level quartet terms. However, the lowest term in the quartet system, namely, the b^4P term of the sp^2 configuration, was not located. Table I lists several multiplets that represent combinations between the previously identified high level terms and this b^4P term. This gives the term values shown in the table, relative to Fowler and Selwyn's quartet system.

Table I. *Multiplets in C II.*

Int.	λ	ν	Series designation	Term values
2	641.62	155855.	$b^4P_{1,1,2}-3d^4P_{1,2,1}$	b^4P_1 206810.7
3	641.84	155802.	$b^4P_{2,3,3}-3d^4P_{3,2,3}$	b^4P_2 206789.2
				b^4P_3 206760.6
4	651.36	153525.	$b^4P\ \ -3d^4D$	
				c^4S 107788.1
5	806.400	124007.9	$b^4P_2\ \ -3s^4P_3$	
5	806.570	123981.8	$b^4P_{1,3}\ -3s^4P_{2,3}$	
4	806.862	123936.9	$b^4P_{2,3}\ -3s^4P_{1,2}$	

Unfortunately, no inter-combinations between the doublet and quartet system have been identified. This makes it impossible to fix accurately one system of values relative to the other. The relation between the two systems is particularly uncertain in this case as all of the known doublet series converge to the 2^1S term of the C^{++} ion, while all of the quartet series converge

[1] Fowler and Selwyn, Proc. Roy. Soc. **A120**, 312 (1928).

to the 2^3P term. This difference is also uncertain because of the failure to find inter-combinations in C III. However, a study of the C III spectrum indicates that the difference between these terms is of the order of 34000 cm^{-1}. If this value is assumed, then the difference between a^2P of s^2p and b^4P of sp^2 is $34000+196659-206811=23848$. This may be in error by as much as 5000 cm^{-1} however.

The inter-combination multiplet (a^2P-b^4P), arising from a transition between these terms, is practically forbidden in a light element such as carbon and, therefore, it has never been observed in a terrestrial source. However, it should appear under nebular conditions and it may be partially represented in the nebular spectrum by some of the unidentified faint lines near 4700A, as some of the expected frequency separations appear in this group.

TABLE II. *Multiplits in N II.*

Int.	λ Vac.	ν	Series Designation	Int.	λ Air	ν	Series Designation
1	475.88	210137.	a_2P-4d^3D	0	4712.13	21215.91	$3p^5D_3-3d^5D_3$
				2	4718.43	21187.58	$3p^5D_2-3d^5D_2$
2	529.37	188904.	$a^3P_{1,0}-3d^3P_{0,1}$	0	4721.59	21173.40	$3p^5D_1-3d^5D_2$
2	529.63	188811.	$a^3P_1-3d^3P_2$				
2	529.83	188740.	$a^3P_2-3d^3P_3$	2	4991.22	20029.61	$3s^5P_2-3p^5P_2$
				0	4997.23	20005.52	$3s^5P_1-3p^5P_1$
3	582.157	171775.0	a^1D-3d^1D	2	5012.026	19946.46	$3s^5P_{2,1}-3p^5P_{2,1}$
				2	5023.11	19902.45	$3s^5P_2-3p^5P_2$
2	629.19	158935.	$b^5S-3s^5P_2$				
2	629.44	158871.	$b^5S-3s^5P_3$	1	5168.24	19343.57	$3p^5P_1-3d^5D_2$
				1	5170.08	19336.61	$3p^5P_1-3d^5D_1$
2	635.20	157430.7	a^1S-3d^1P	1	5171.46	19331.53	$3p^5P_2-3d^5D_2$
				1	5172.32	19328.32	$3p^5D_1-3d^5F_2$
3	660.291	151448.4	a^1D-b^1P	2	5173.37	19324.39	$3p^5D_2-3d^5F_3$
				1	5174.46	19320.32	$3p^5P_3-3d^5D_3$
3	745.839	134077.2	a^1S-b^1P	3	5175.89	19314.98	$3p^5D_3-3d^5F_4$
				5	5179.50	19301.52	$3p^5D_4-3d^5F_5$
4	746.989	133870.8	a^1D-3s^1P	2	5183.21	19287.71	$3p^5P_2-3d^5D_2$
	Air			2	5184.97	19281.16	$3p^5D_2-3d^5F_3$
1	4124.10	24240.90	$3s^5P_1-3p^5S$	2	5190.42	19260.91	$3p^5D_3-3d^5F_4$
2	4133.654	24184.87	$3s^5P_2-3p^5S$	00	5199.53	19227.17	$3p^5D_4-3d^5F_5$
3	4145.759	24114.26	$3s^5P_3-3p^5S$				
				2	5526.26	18090.41	$3s^5P_1-3p^5D_2$
1	4695.91	21289.19	$3p^5D_1-3d^5D_2$	4	5530.27	18077.29	$3s^5P_2-3p^5D_3$
0	4700.12	21270.12	$3p^5D_2-3d^5D_3$	5	5535.39	18060.57	$3s^5P_3-3p^5D_4$
0	4702.57	21259.04	$3p^5D_3-3d^5D_4$	1	5540.16	18045.02	$3s^5P_1-3p^5D_2$
0	4704.33	21251.09	$3p^5D_2-3d^5D_2$	3	5543.49	18034.18	$3s^5P_2-3p^5D_2$
0	4706.41	21241.70	$3p^5D_3-3d^5D_3$	3	5551.95	18006.70	$3s^5P_2-3p^5D_3$
				0	5565.30	17963.51	$3s^5P_3-3p^5D_2$

Term Values

a^1D	223529	$3p^5S$	65759.0	$3d^5D_1$	50658.5
				$3d^5D_2$	50650.6
a^1S	206157	$3p^5P_1$	69994.6	$3d^5D_3$	50639.3
		$3p^5P_2$	69970.7	$3d^5D_4$	50624.9
		$3p^5P_3$	69926.9		
				$3d^5F_1$	52611.4
		$3p^5D_2$	71955.0	$3d^5F_2$	52585.3
		$3p^5D_1$	71939.8	$3d^5F_3$	52551.6
$3s^5P_1$	90000.0	$3p^5D_3$	71909.6	$3d^5F_4$	52511.1
$3s^5P_2$	89943.8	$3p^5D_2$	71866.5		
$3s^5P_3$	89873.1	$3p^5D_4$	71812.6		
				b^5S	248812.

SPECTRA OF N II

Fowler and Freeman[2] analyzed the triplet and singlet systems of N II but they failed to locate the a^1S and a^1D terms of the s^2p^2 configuration. The identification[3] of the 6548 and 6583 nebular lines fixed the a^1D term and

[2] Fowler and Freeman, Proc. Roy. Soc. **A114**, 662 (1927).

[3] Bowen, Astrophys. J. **67**, 1 (1928).

Becker and Grotian's[4] provisional identification of the 5755 line from its behavior in the nebulae indicated the position of the a^1S term. If we assume these values, we can at once predict the position of the lines arising from the combinations between these terms and the high level singlet terms found by Fowler and Freeman. The observed lines, identified by their close agreement with the predictions, are given in Table II. As the deviations between the predicted and observed wave-lengths are in every case well within the experimental error, little doubt remains as to the correctness of the identification of these nebular lines.

Fowler and Freeman did not locate any of the quintet terms that appear when one of the *s* electrons is excited. However, several multiplets were found and designated with an *a*, which they thought were triplets, although they were unable to fit them into the general N II system of terms. Further study shows that other lines in the region of these multiplets belong to them and that they are in reality quintets. These completed multiplets along with several additional multiplets belonging to the same quintet system are listed in Table II. All of the wave-lengths above 2000A are taken from Fowler and Freeman, while the shorter wave-lengths represent new determinations The preceding small letters and numbers indicate the position of the excited electron.

The term values of the singlet terms are relative to Fowler and Freeman's system. The quintet terms are independently fixed, as no inter-combinations have been found. They differ from the values of the triplets and singlets by approximately the amount that b^4P of the sp^2 configuration of N III differs from the a^2P term of s^2p configuration, as these are the terms to which the respective series converge.

[4] Becker and Grotrian, Ergebnisse der Exackten Naturwissenschaften, **7**, 65 (1928).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eight of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

The Capture of Electrons by α-Particles

Davis and Barnes report (Phys. Rev. **34,** 152; July 1, 1929) that the capture of electrons by α-particles occurs not only when the accelerating voltage, V_0, is such as to give the electrons the same velocity as the α-particles, but also for a double series of values, V_n, satisfying the equation: $E_n=(V_0^{1/2}-V_n^{1/2})^2$, where E_n is the ionizing potential of He^+ in the n^{th} quantum state. They give, however, no mechanism for the effect.

As a two-body problem the effect is difficult to explain, but there is no reason for limiting oneself to the two body case. Henderson has shown (Proc. Roy. Soc. (London) **A109,** 157, 1925) that a beam of α-particles which has passed through matter contains He^+ ions, the ratio He^+/He^{++} depending on the velocity but not on the material. Consider a collision of a He^+ ion in the n^{th} quantum state with an electron accelerated by a potential approximately satisfying the equation above. The He^+ ion will be ionized, the products of the collision being an α-particle,—He^{++},—and two electrons practically at rest with respect to the stream of α-particles. The electrons will therefore be captured, giving *two* He^+ ions of high quantum state. When, by radiation, they have reached the n^{th} quantum state, they will be again ionized, giving *four* electrons, which upon capture give *four* He^+ ions. The process is therefore cumulative.

If more than half the He^+ ions skip the n^{th} quantum state, or pass through it without suffering an ionizing collision, the process will cease to maintain itself. This appears to have happened, under the conditions of Davis and Barnes, experiments, for $n>11$.

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July 19, 1929.

PROCEEDINGS OF THE AMERICAN PHYSICAL SOCIETY

MINUTES OF THE BERKELEY MEETING, JUNE 21 AND 22, 1929.

The 158th regular meeting of the American Physical Society was held in Berkeley, California, in conjunction with the meetings of Section B of the Pacific Division of the American Association for the Advancement of Science, Friday and Saturday, June 21st and 22nd, 1929. The Friday morning session was held in Room 1, Students' Observatory of the University of California, and the afternoon session on Friday, and the Saturday session were held in Room 210, Le Conte Hall. The Friday morning session which consisted of a joint session with the Astronomical Society of the Pacific in which there were five papers by invitation, was presided over by Dr. Walter G. Adams, President of the Pacic Division of the American Association for the Advancement of Science. The Friday afternoon and Saturday morning sessions were presided over by Professor E. E. Hall, Chairman of the Physics Department of the University of California. The papers presented in the joint session with the Astronomical Society of the Pacific are as follows:

1. **The theoretical intensities of emission and absorption lines**—D. H. MENZEL, *Lick Observatory.*
2. **Probable values of the general physical constants**—R. T. BIRGE, *University of California.*
3. **A photographic study of the solar spectrum in the region 10,000–11,000A.**—H. D. BABCOCK, *Mount Wilson Solar Observatory.*
4. **The chemical composition of gaseous nebulae.**—I. S. BOWEN, *California Institute of Technology.*
5. **Elements not yet identified or questionable in the atmosphere of the sun.**—C. E. ST. JOHN, *Mount Wilson Solar Observatory.*

Following this session there was a joint luncheon for members of the Astronomical Society of the Pacific and the American Physical Society at the Women's Faculty Club, with forty members attending. Preceding the regular presentation of papers on Friday afternoon, a short business meeting was held in which the following matters were discussed:

Owing to difficulties in the reception of abstracts by the Secretary on Saturday afternoon, it was moved, seconded, and voted, that the time for the reception of the abstracts by the Pacific Coast Secretary of the Physical Society be changed to Friday, a month preceding the date of meeting, instead of Saturday a month preceding the meeting as heretofore.

It was moved, seconded, and voted, that the meeting of the Physical Society held in December on the Pacific Coast would not permit the Physical Society participating in the general session of the Pacific Division of the

American Association for the Advancement of Science in the event of a meeting held in the fall, winter or early spring. The summer meeting will as usual be held in affiliation with Section B of the Pacific Division of the American Association as heretofore. It was moved, seconded, and voted, to recommend to the executive committee of the Physical Society that the date of the 160th meeting of the American Physical Society which is to be held at Stanford University, be on Saturday, December 7, 1929, with the possible view to the necessity of extending the meeting from Friday, December 6, at 2:00 P.M., through Saturday, December 7, 1929, owing to the length of the progarm during the last meeting on the Pacific Coast. The regular program of the American Physical Society consisted of forty-two papers. Papers numbers 7, 14, 19, 22, 23, 24, 33, 34, and 36 being read by title.

The abstracts of the papers are given in the following pages. An **Author Index** will be found at the end.

L. B. LOEB,
Secretary for the Pacific Coast.

ABSTRACTS

1. A new titanium band system. ANDREW CHRISTY, *University of California.*—Using chiefly previously published data, the writer has found a new system of titanium monoxide containing 18 bands, whose lower level is the same as that of the known blue-green bands. This new system has apparently been found, independently, by F. Lowater. Both systems appear in absorption in stellar spectra, proving that the two are resonance systems. Five unassigned bands found by Shane in o Ceti are shown to belong to the new system. The frequency of the heads is given by

$$\nu = \left.\begin{matrix}14172.2\\14105.8\\14030.8\end{matrix}\right\} + (862.5n' - 3.84n'^2) - (1003.8n'' - 4.61n''^2)$$

with an average residual of one cm^{-1}. The mean separation of the heads is 70.7 cm^{-1}, a value obtained indirectly for the lower level of the blue-green system. The upper level of the new system is in all probability a ^3S. The bands of TiO persist in stellar spectra up to temperatures of about 3500°T. Applying the Sackur-Tetrode equation, and assuming—first, the heat of dissociation for the lower level is 6.74 volts; second, if the ratio of Ti to TiO is as 100 to 1, the bands will not be observable,—we find that in stellar atmospheres the partial pressure of oxygen is 10^{-6} atmosphere.

2. The vibration spectrum of the ammonia molecule. JOSEPH W. ELLIS, *University of California at Los Angeles.*—The infra-red absorption spectrum below 2.5μ of NH_3 in CCl_4 and aqueous solutions and the visible spectrum of the latter solution have been obtained. Bands, decreasing in intensity with increasing frequency, at 1.51, 1.035, 0.795, 0.652 and 0.556μ fit the formula $\nu_n = 97 + 3400n - 70n^2$, the variable portion of which is the equation of an anharmonic vibrator. Extrapolation of this series indicates the 2.916μ band of Robertson and Fox (Proc. Roy. Soc. **120**, 168 (1928)) as a fundamental. Evaluation of the dissociation energy of the oscillator yields 5.1 equivalent volts in sufficient agreement with the energy of a single N-H bond to identify the oscillator as an N-H pair of atoms. Other bands observed in CCl_4 solution were: 2.35, 2.29, 2.01, 1.655, 1.29 and 1.21μ; and in aqueous solution: 1.62, 1.29, 1.21 and 0.733μ. Comparison of these bands with those observed in gaseous NH_3 by Robertson and Fox indicates only slight wave-length shifts, if any, on account of solution. The whole vibration spectrum of the ammonia molecule can be correlated on the basis of three fundamental bands: 10.55, 6.132 and 2.916μ. The 3μ absorption region is really double, including the last named fundamental and the first overtone of the 6.132 band.

3. Intensities in super-multiplets of titanium. GEORGE R. HARRISON, *Stanford University.*—Quantitative measurements have been made on the quintet pentadtriad super-multiplet of Ti I, which contains 10 multiplets arising from the transition $[(3d)^24s]\,4d-4p$. The 35 sets of spectrograms reduced show very good agreement, although most of the lines are very weak. A large majority of the lines are of anomalous intensity, and the sum rule does not hold within the individual multiplets, and only slightly better for the super-multiplet as a whole. Four relatively strong ^5FH lines appear to have obtained their energy, in part, by robbing ^5GH lines having the same upper states. When all known inter-system combinations are added in, and when the J values corresponding to given L values are added together, Kronig's formulas and the sum rule are approximately obeyed. This super-multiplet appears to furnish the most anomalous set of intensities yet observed; its intervals are also anomalous, and the lines are nebulous in sources at moderate pressures. No self-reversal affected the results, as was shown by simultaneously photographing the triad super-multiplet $^5F'-{}^5G'FD'$ $[(3d)^24s]\,5s-4p$, which has the same lower states as the other. These multiplets are practically normal, and their intensities came out within 5 percent of the theoretical 9:7:5, no excitation correction being necessary.

4. Characteristics of the electric furnace spectra of europium, gadolinium, terbium, dysprosium and holmium, λ3900–λ4700. ARTHUR S. KING, *Mount Wilson Observatory.*—Two objects in a preliminary study of these spectra were the separation of the lines arising respectively from the neutral and ionized atoms, and the temperature classification of both groups. The first was carried out by the usual comparison of arc and spark spectra, but the selection was confirmed and many critical cases decided by the method of mixture in the tube-furnace with a substance of low ionization potential such as caesium, which by contributing a large supply of free electrons promotes recombination and quenches the ionized lines. The temperature classification was based on spectra for three furnace temperatures between 2000° and 2800°C and a comparison with the arc spectrum. Groups of very strong low-temperature lines were noted, especially for europium, dysprosium and holmium, and as in previous studies of rare earths the furnace was found to emit strongly many lines which are faint in the arc and hitherto unidentified. Hyperfine structure, previously noted for lanthanum and praseodymium, was found for many lines, usually ionized, in the spectra of europium, terbium and holmium. In graduated spacing of components these often resemble the lines of ionized praseodymium.

5. Low energy states in C_{II} and N_{II}. I. S. BOWEN, *California Institute of Technology.*—Several of the strong lines of C_{II} have been identified as combinations of the ^4P term of the sp^3 configuration with the quartet terms observed by Fowler and Selwyn (Proc. Roy. Soc. **120**, 212). This fixes the term values $^4P_1=206810.7$, $^4P_2=206789.2$, $^4P_3=206760.6$. In N_{II}, the term value of the ^1S term of the s^2p^3 configuration, has been fixed at 206159, and of the ^1P term of the sp^3 configuration at 72084. relative to the term values given by Fowler and Freeman (Proc. Roy. Soc. 114, 662). The ^1S term combines with the ^1D term of the same configuration to give the nebular line at 5754.8A. A large number of terms including those which Fowler and Freeman designated by "a" have been shown to belong to the quintet system. These have the following relative term values: sp^2s, $^5P_1=90000$, $^5P_2=89943.8$, $^5P_3=89873.1$; $sp^2\cdot p$, $^5S=65759.0$, $^5P_1=69994.6$, $^5P_2=69970.7$, $^5P_3=69926.9$, $^5D_0=71955.0$, $^5D_1=71939.8$, $^5D_2=71909.6$, $^5D_3=71866.5$, $^5D_4=71812.6$; $sp^2\cdot d$, $^5D_1=50658.5$, $^5D_2=50650.6$, $^5D_3=50639.3$ $^5D_4=50624.9$, $^5F_2=52611.4$, $^5F_3=52585.3$, $^5F_4=52551.6$, $^5F_5=52511.1$; sp^3, $^5S=248812(?)$.

6. Relative abundance of the isotopes of oxygen. HAROLD D. BABCOCK, *Mount Wilson Observatory.*—Improved agreement is found between observed positions of lines of the A' band and those calculated for the isotopic molecule $O^{16}-O^{18}$, the average residual being -0.02 cm^{-1}. The existence of O^{18} is further confirmed by the occurrence in A' of 34 lines corresponding to odd numbered rotational levels not recognized in the original description of the band, and also by another new faint band, B', likewise showing both sets of levels and displaced 30 to 40 cm^{-1} from the B band. A third exceedingly weak band, A'', is described, which Giauque and Johnston have attributed to another molecule, $O^{16}-O^{17}$. Their conclusion is confirmed and from the intensities of the lines it is estimated that O^{16} is roughly 10000 times as abundant as

O^{17}. On photographing the A and A' bands with air paths of a few meters and of several kilometers respectively they were made to appear of equal intensity. The actual ratio of intensities thus found is 1250:1. This would make the relative abundance of atoms O^{16} and O^{18} 2500:1, but since the A' band has twice as many rotational states as the A band the ratio remains 1250:1.

7. The Raman effect in water. E. L. KINSEY, *University of California at Los Angeles.*—The light of a glass mercury arc scattered by distilled water at room temperature was photographed on astronomical green sensitive plates. Exposures of 24–36 hrs. yielded three scattered bands which are to be designated as the "4150 band," the "4680 band" and the "5157 band." The 4150 band is a doublet excited by the 3650 mercury line and the 4680 band, a triplet excited by the mercury pair 4046 and 4077. These bands can be accounted for by two infra-red wave-lengths 2.92μ and 3.13μ whose existence Ellis has also postulated in order properly to correlate the infra-red spectrum.

	Scattered wave-length	Exciting line	Infra-red scattering frequency
"4150"	4126 (24237)	3650 (27398)	3.16μ (3161)
	4158 (24050)	3650 (27398)	2.98μ (3348)
"4680"	4647 (21520) strong	4046.6 (24712)	3.13μ (3192)
		4046.6 (24712)	2.92μ (3417)
	4696 (21295) very strong	4077.8 (24538)	3.09μ (3233)
	4737 (21100)–weak	4077.8 (24528)	2.92μ (3417)

The centers of the 4680 band can be determined within 5A introducing an error of about 25 cm^{-1} and about 0.04μ in the infra-red scattering wave-length. In addition 4647 would also coincide with a band from the mercury line 4358 scattered by 6.31μ of which 3.13μ is the first harmonic. The fact that 6.31μ does not produce Raman scattering or if so, so feebly as to escape detection, is indicated by the absence of the 4180 triplet when the exciting light contained only the 4358 mercury line, 4046 and 4077 being removed by a suitable filter.

8. Relative intensities of lines in a generalized multiplet of Ti II. HARRY ENGWICHT, *Stanford University*—The multiplet $a^4P'-a^4D'[(3d)^2]3d-4p$ of Ti II has been shown by Harrison to have extremely anomalous intensities. Measurements have been made on this and the related multiplet $a^2P'-a^2D'$, together with their inter-system combination lines, many of which are strong. The quartet, doublet and their inter-system lines form a generalized multiplet (Ornstein and Burger's "Erweiterte Multiplett"). A titanium vacuum arc was used as a source, the necessary self-reversal correction being small. Measurements were made using the second order of a ten meter concave grating, more than fifty exposures being used. When an excitation correction corresponding to 3500°A is applied the total intensities of quartet to doublet are found to have the theoretical ratio 2:1. The sum rule is more closely approached when the inter-comb nation lines are included in the sums than when they are omitted, but the lack of agreement is still many times the experimental error. The results indicate that this group of lines must be considered in conjunction with the remainder of a still more general group; perhaps that group containing their remaining members of the generalized super-multiplet of which this is a part.

9. The recombination of ions and of ions and electrons in gases. LAURISTON C. MARSHALL, *University of California.* (*Introduced by Leonard B. Loeb.*)—Using a method described in a previous paper (Phys. Rev. **33**, 266 (1929)), the recombination coefficient, α, in air is found to vary with the x-ray exposure, t', and the recombination time, t, and is consequently also a function of the initial ion concentration, n_0. α decreases with increase of the above quantities and approaches a constant value between 0.8 and 0.9×10^{-6}. Explanation is based on the assumption that the ions are initially distributed in pairs along the paths of the x-rays leading to fictitiously high calculated values at short time intervals. This lends support to

J. J. Thomson's theory that diffusion plays the major role in the initial stages of the mechanism. In argon, where electrons remain free for appreciable intervals, α takes on a nearly constant value less than half that expected on the kinetic theory basis. Rapid achievement of random distribution when free electrons are present, accounts for the constancy. The value agrees qualitatively with spectroscopic results of Kenty and indicates a low rate of recombination between electrons and positive ions. α, as observed here, is not a true measure of the recombination process, but serves as an indication of the rate of negative ion formation through attachment of electrons to impurities present.

10. The theory of recombination of gaseous ions. LEONARD B. LOEB AND LAURISTON C. MARSHALL, *University of California.*—The bearing of the recent results of Marshall on the theory of recombination of gaseous ions is discussed. It is shown, by solution of the Brownian movement equation for two ions of opposite sign in a gas, that the average relative displacement in a time t is little influenced by the attractive forces, except for distances of the order of magnitude of 10^{-5} cm or less at ordinary temperatures. This conclusion, that in general the motion of the ions relative to each other is largely one of random diffusion, is in good agreement with the interpretation forced by Marshall's study of the variation of the coefficient of recombination α with time and concentration of ions. This also indicates that the theoretical approach of Langevin to the solution of the recombination problem is untenable, while that of Thomson is justified. The theoretical evaluation of the coefficient α, using Thomson's approach, is discussed and is compared with observation. It appears to fit qualitatively as accurately as the facts are known. It is then shown how the success of any theoretical treatment is limited due to our ignorance of the nature of the mass of the ion, a condition which, however, enables us to understand the very small range of variation of α among the different gases.

11. Intermolecular attractions in liquids. J. H. HILDEBRAND, *University of California.*—The volume energy of a liquid is formulated in terms of inverse power attractive and repulsive forces. The expression thus obtained is introduced into the thermodynamic equation of state. The general equation resulting is shown to meet several severe tests with a number of normal liquids.

12. Relative probabilities of the ionization of K and L series electrons of equal ionization energy. GERALD L. PEARSON, *Stanford University.* (*Introduced by D. L. Webster.*)—The probability that an atomic electron will be ejected by a cathode ray depends at least on the ionization potential and the energy of the cathode ray; it may depend also on quantum numbers. Between the L_{11} and the L_{21} states there are inverse changes in radial and azimuthal numbers; a K electron is like L_{11} in azimuthal and L_{21} in radial. The present experiments are on rays from PbSe, where the Se K electrons have nearly the same excitation energy as the Pb L_{22}. Assuming first that every ionization results in radiation of some line of the appropriate series, the relative probabilities of ionization were calculated from the observed line intensities, corrected for differences of excitation voltages. The number of Se K ionizations is nearly that of Pb L_{21} but far greater than Pb L_{11}. This indicates that the probability of ionization varies with the radial quantum number, rather than the azimuthal. Since some atomic reorganizations result in secondary photoelectrons, and the term efficiency of emission signifies the probability that a reorganization will result in radiation, the above ratios are really those of products of probabilities of ionization by efficiencies of emission.

13. A new method of measuring the thermal conductivities of gases. E. D. MCALISTER AND H. J. YEARIAN, *University of Oregon.*—By placing a sensitive thermocouple at the center of a spherical shell a radial flow of heat from the receiver of the couple through the intervening gas to the inner wall of the shell is accomplished. This arrangement is free from boundary corrections. The temperature difference between the couple and the walls is 1°C or less thus practically eliminating convection currents. The coefficient of conductivity for ordinary pressures is given by

$$k = L_v \left[\frac{i_v}{i_p} - 1 \right] \frac{r_2 - r_1}{4\pi r_1 r_2},$$

where L_v = heat loss from thermocouple in vacuo (10^{-5} mm Hg), i_v = current from thermocouple when in vacuo, i_p = current from thermocouple when in a gas at pressure p, r_2 = radius of shell, r_1 = radius of a sphere equivalent to the receiver of the couple. Experimental values obtained at atmospheric pressure and 20°C are for dry air, $k = 5.86 \times 10^{-5}$ cal cm^{-2} sec^{-1} deg^{-1}; H_2, $k = 3.87 \times 10^{-4}$; O_2, $k = 5.95 \times 10^{-5}$, and CO_2, $k = 3.78 \times 10^{-5}$ (at 0°C). This value for CO_2 gives 1.70 for $k/7C_v$ which compares favorably with Jeans' value 1.72.

14. Field of view of secondary image, with point-object stationary, for two independently variable plane mirrors having limited widths. L. E. DODD, *Department of Physics, University of California at Los Angeles.*—Optical system composed of two plane mirrors variable about parallel axes, $A \equiv (d, O)$, $A_0 \equiv (O, O)$, situated in the respective planes, point object $O \equiv (x_0, y_0)$, forms secondary image, O'', in polar coordinates located at $\rho = f(x_0, y_0, d, \xi)$, $\phi = f(\rho, \eta)$, ξ and η being slope-angles of M_1, M_2. [L. E. Dodd, J.O.S.A. & R.S.I., *17*, 369 (1928). (Minor change has been made in subscript of symbols.)] These eqs. used in the oclinometer, developed by Liggett and Dodd, and described elsewhere. Further problem, "field of view," $\Delta\sigma = [(\sigma_3)_2 - (\sigma_3)_1]$, of O'' to eye at $E \equiv (x_3, y_3)$. σ's are slope-angles of two limiting emergent rays, both determined by outer edge of M_1, $A_e \equiv (x_e, y_e)$. Direction of $\Delta\sigma$, $\sigma_v = [(\sigma_3)_1 + (\sigma_3)_2]/2$. $(\sigma_3)_1$ obtained from θ_1 by (1) $\sigma_3 = f(\xi, \eta, \theta)$, (2) $\eta = f(d, y_0, \xi, x_e, y_e, x_3, y_3, x_1, y_1)$, where $\theta \equiv$ angle AOB_1, $\tan\theta = (d - x_1)/(y_1 - y_0)$. $(\sigma_3)_2$ known already. Desirable to find θ_2. But reverse solution $[\theta = f(\sigma_3)]$ of (1), (2), less practicable. However, θ_2 obtainable from $(\sigma_3)_2$ by (1) above, (3) $\eta = f(\xi, \phi, \alpha, \psi)$ (previous paper), (4) $\phi = f(\sigma_2, \rho, x_3, y_3)$. Again, reverse solution $[\sigma_3 = f(\theta)]$ of (1), (3), (4), impracticable. Other general expressions given: slope-angles of "incident" and "transmitted" ray-segments, OB_1, B_1B_2; incidence-points, $B_1 \equiv (x_1, y_1)$, $B_2 \equiv (x_2, y_2)$, of ray on M_1, M_2, (useful areas of mirrors from these); incidence-angles; deviations; η. All eqs. applied to rays limiting $\Delta\sigma$. Effects on $\Delta\sigma$, σ_v, of parameters ξ, d, y_0, x_3, y_3. Present conditions $[x_0 = d,\ \xi = 160° = const.,\ \eta$ variable, $d = 9$ cms., width of M_1 2.3 cm, of M_2 8.0 cm, O'' above x-axis] permit $-20 > y_0 > -\infty$ cm (upper limit here provides approximately distance most distinct vision), with corresponding $47° > \Delta\sigma > 41°$, and $90° < \sigma_v < 93°$ approximately, giving to desirable degree, constancy of $\Delta\sigma$, σ_v.

15. A new graphical arrangement of the periodic table. A. E. CASWELL, *University of Oregon.*—The chemical elements are represented by points on a spiral plotted on polar coordinate paper. The atomic numbers are used as radial coordinates. Successive elements, in general, are plotted at angles 20° apart. Thus, the inert gases lie on the radial line $\theta = 0$, the alkali metals on $\theta = 20°$, the alkaline earth metals on $\theta = 40°$, the halogens on 340°. Beryllium and magnesium are on the 40° line, while boron and aluminum are on the 260° line, adjacent to carbon and silicon, respectively. The rare earth elements are all placed together on the 60° line. The so-called transition groups (Fe, Co, Ni, etc.) fit into the chart naturally. The metals and non-metals divide the chart into two compact areas. Periodic properties of the elements are easily shown on the chart. For example, basicity increases with increase in radius, but decreases with increase in angle. High atomic volumes lie at the right, low at the left. At the right, relationships are radial rather than tangential, but toward the left tangential relationships become more pronounced.

16. A projection lantern microphotometer. CEDRIC E. HESTHAL AND GEORGE R. HARRISON, *Stanford University.*—The photographic plate to be measured is mounted in screw-controlled vertical and horizontal ways in a projection lantern, and a photoelectric cell is placed behind an adjustable slit in the projection screen. The current from the cell is amplified by a two-tube Wheatstone bridge circuit of the Wynn-Williams type. A micro-ammeter or quick acting galvanometer is used as the recording instrument, and the system is extremely sensitive, stable, and readily controlled. A potential of only six to twenty volts is used on the photoelectric cell and on the leak cell, to reduce fatigue. The advantages of this type of microphotometer are: (1) a large field of the plate is visible at all times, so flaws in the emulsion can be avoided and lines can be set on very accurately; (2) the resolving power can be quickly made extremely high or low as desired; (3) an extremely quick acting but stable in-

strument can be used for recording; (4) 10-fold changes in sensitivity can be quickly made to increase accuracy for very high densities; (5) the scale of the apparatus is such that errors due to handling and adjustment are minimized.

17. Apparent modulation of light by films of dielectrics on cathodes of alkali metal photoelectric cells. A. R. OLPIN, *Bell Telephone Laboratories.*—Cathodes of alkali metal photoelectric cells have been highly sensitized to light by the use of small amounts of various dielectrics. Changes in the shape of the spectral response curve are attributed to modulation of the frequencies of the incident light upon absorption. Differentiation is made between the incident light frequency and the exciting frequency. If light of frequency p is incident on a film of dielectric having vibration-rotation frequencies q, new frequencies $p \pm q$, $2p \pm q$ will appear to liberate electrons whenever such frequencies fall in the spectral region to which the alkali metal responds. The summation frequencies appear to be almost insignificantly small. Modulation of the incident beam to give the $p-q$ frequency is apparently responsible for the increased response to light of short wave-lengths, while the $2p-q$ frequencies cause a new maximum to appear at longer wave-lengths. Experimental data are shown which confirm these theoretical considerations. Work with subharmonics in non-linearly coupled electrical circuits offers an analogy. Variations in Einstein's equation for different spectral regions are indicated if the incident light is modulated.

18. Multiple processes in the x-ray region. R. M. LANGER, *National Research Fellow, Bureau of Standards.* S. B. HENDRICKS, *Bureau of Chemistry and Soils, Department of Agriculture.*—I. B. B. Ray and R. C. Mazumdar (Zeits. f. Physik **53,** 646 (1929)) postulated the existence of simultaneous multiple electron transitions in a particular atom as an explanation for the numerous excitation potentials in the soft x-ray region. The data are in better agreement with the idea that the process is one of consecutive collisions of a single electron with separate atoms rather than the one mentioned above. Such a process is, moreover, inherently more plausible than the first. H. Coster and Druyvesteyn (Zeits. f. Physik **40,** 265 (1927)) and more recently F. K. Richtmyer (Phil. Mag. **6,** 68 (1928)) have explained the appearance of certain x-ray non-diagram lines as being produced by simultaneous electron jumps in a multiply excited atom. A class of such satellites, appearing as a rule on the low frequency side of the diagram line and near to it, can possibly be explained as arising from single electron transitions in atoms, the levels of which have been altered by modifications in the configurations of the outer electrons of the atom. Considerable qualitative evidence supports this postulate. Approximate calculations of charge distribution, using crude hydrogen-like wave functions, show that the screening effect of the outer electrons is of the required order of magnitude.

19. Thermal expansion of tantalum. PETER HIDNERT, *Bureau of Standards.*—Data on the linear thermal expansion of three samples of worked and annealed tantalum over various temperature ranges between $-190°$ and $+500°$C, have been obtained. These samples were nearly pure (99.9+ percent). Two types of expansion apparatus were used in this investigation. A summary of available data by previous observers on the thermal expansion of tantalum was prepared. Worked tantalum was found to expand practically the same as annealed tantalum. The following equation is given as the most probable second-degree equation for the expansion of tantalum between 20° and 500°C:

$$L_t = L_0 [1 + (6.59t + 0.00008t^2)10^{-4}].$$

The complete results have recently been published in Bureau of Standards Journal of Research **2,** 887 (1929).

20. Features of the furnace, arc and spark spectra of hafnium. ARTHUR S. KING. *Mount Wilson Observatory.*—The spectrum of hafnium, given by the metal in the carbon-tube furnace, has been examined from $\lambda 2650$ to $\lambda 6500$ and compared with the spectra of the arc and spark. The temperature classification of 337 lines within this range and the selection of ionized lines are based on the data from the three sources. The vaporization point of the metal being high, an initial temperature of 2600°C was required for the furnace spectrum, and 2900° was used as

a higher stage. No ionized lines were given by the furnace, and relatively few neutral lines appear at the lower temperature. The arc and spark spectra show decided differences in the excitation required for different groups of enhanced lines, and some of these may belong to the second ionization. A system of bands, each degraded toward the red, is distributed between λ3200 and λ5700. Their occurrence in the arc in air and their absence in the vacuum furnace point to the oxide as a probable origin.

21. An electric vacuum furnace for quantitative line intensity determinations. GEORGE R. HARRISON, *Stanford University.*—The unknown magnitude of the excitation correction often causes great uncertainty in interpreting line intensity determinations. The classical work of A. S. King with the electric furnace suggests the desirability of having such pure temperature excitation for quantitative intensity work. The disadvantages of the furnace are self-reversal, comparatively long exposures required, and greater background intensity. A furnace based on King's has been built, with modifications designed to reduce self-reversal and increase ease of handling. Base plate and cover are of tinned bronze, water-cooled externally and fastened together with soft wax. The graphite tube is so mounted that it can be removed and inserted through the end windows of the cover, making reloading a quick process. A slit in a thin graphite disk is placed near one end of the heating tube. This reduces diffusion of cooler vapor into the line of sight, and furnishes a radiation standard at the vapor temperature. Satisfactory spectrograms are obtained with the 10 meter grating in one to five minutes. Self-reversal remains in Class I and II lines, but experiments are in progress designed to reduce this by washing diffusing vapor to one side of the slit with a blast of hot gas.

22. A heavy electromagnetic pendulum for use as a self-regulating motor. L. E. DODD, *Department of Physics, University of California at Los Angeles.*—A heavy physical pendulum, approximate dimensions, length 155 cm (to center of bob), amplitude 31 cm, wt. 35 lbs. period 2.4 sec, is driven by four electromagnets, solenoid-plunger type, placed vertically in pairs tandem-fashion. Coils are No. 28 d.c.c. Cu wire, averaging roughly 5500 turns each. Energy fed to pendulum by good quality cord (fishline) passing from plungers, over light pulleys, to main support-rod at a point about ⅓ length of pendulum from point of support. Two solenoids work half-time and two quarter-time, pendulum receiving energy practically continuously. Special make-and-break device distributes current of less than 1 amp. from 135-v. d.c. source. Wattage includes appreciable heating of solenoids. Pendulum regulates automatically its own amplitude. Separate wiring system for relay to minimize sparking at Hg contacts, but this is controllable by condensers. Present apparatus drives an aluminum lever 0.6×1.8×110 cm, imparting up-and-down motion to sieve-like stirrer for work on miscibility of liquids. End of lever opposite stirrer passes somewhat loosely through rectangular aperture in brass slip, running in vertical guides, which is part of another cord-system, with pulleys, attached symmetrically to center of lens-shaped lead bob (26½ cm diam.) by means of two horizontal forks. Apparatus works smoothly for indefinite period.

23. Recombination of atoms. E. L. KINSEY AND JOSEPH KAPLAN, *University of California at Los Angeles.*—The shapes and relative positions of the Franck-Condon potential energy curves associated with the normal and excited levels of a diatomic molecule, determine whether or not it is possible for two atoms on a two body collision to combine into a homo-polar molecule. The following generalization arises, which is in accord with the Franck-Condon postulates. The collision of two atoms can result in the formation of a homo-polar molecule when, and only when the minimum energy in an excited state of the molecule is equal to or less than the heat of dissociation of the normal molecule. Three such cases arise. The total energy in one or more excited electronic levels of the molecule can be *a*) less than the heat of dissociation (no such case is known); *b*) more than the heat of dissociation (as in N_2 and NO); *c*) equal to the heat of dissociation (as in O_2). In every case the energy of recombination is lost as radiation. When no electronic level possesses an energy less than the heat of dissociation, energy cannot be lost by radiation and recombination by two body collision cannot occur (unless of course conservation of momentum is to be violated). Some other process such as a wall reaction is necessary. Hydrogen is an example of such a case.

24. Transition probabilities. E. L. KINSEY AND JOSEPH KAPLAN, *University of California at Los Angeles.*—The quantum nature of energy changes is expressed by the relation $E=h\nu$. The statement can be made in an altered form which gives rise to a connection between the transition probabilities P, and the time during which a transition takes place Δt. The statement is that $\Delta E\ \Delta t=h$, where ΔE is the energy change occurring during one vibration of the emitting or absorbing mechanism (or what amounts to the same thing, for emission, it is the energy associated with a single emitted wave). If we assume with Heisenberg that the probability of emission is measured by the square of the electric vector the expression for the energy density of electromagnetic radiation gives at once that ΔE is proportional to P/ν. This fact and the first relation show that for a given frequency the most probable transitions occur very rapidly. It seems reasonable to suppose that Δt measures the time during which radiation is emitted without phase change. $c\Delta t$ is then the length of the wave train formed, so that this is also the greatest path difference over which interference can occur. A measure of Δt is thus afforded. The complete relationship, $P\Delta t/\nu=$constant, can now be tested. The $P's$ can be calculated by matrix or wave mechanics methods and Δt estimated by interference experiments.

25. The influence of foreign gases on the intensity of the magnesium 4571 line excited at low pressure. JOHN G. FRAYNE, *California Institute of Technology.*—The 4571 magnesium line, 2^3P_1-1S, appears very faint in the arc at atmospheric pressure. This low intensity is explained by the long life, 10^{-3} sec., of the 2^3P_1 state. In this experiment, magnesium metal at 500°C gave sufficient vapor for a strong electrodeless discharge, using short wave oscillations. At this temperature, the 4571 line appeared fairly prominently in the spectrum. The addition of the noble gases argon, neon, and helium increased the intensity of the line. In the case of argon, the line was increased 100–fold relative to the triplet line 3838 at a partial pressure of around 3 cm. Neon at a pressure of about 1 cm increased the intensity of the line approximately 70–fold while helium raised the intensity about 40 times at 1 cm pressure. Nitrogen caused a gradual increase of intensity up to a pressure around 2 mm. Above this pressure, no discharge could be excited with nitrogen present in the tube. Carbon monoxide behaved similarly to nitrogen. Hydrogen up to a pressure of around 2 mm, caused no increase in the intensity of the line. The 2852 resonance line in general showed a maximum intensity at the lowest pressure of the admixed gas, and diminished gradually with increasing pressure. The sharp and diffuse singlet series diminished in intensity with increasing pressure of the foreign gases.

26. The effect of strong magnetic fields on the formation of bismuth single-crystals. A. GOETZ, R. C. HERGENROTHER AND A. B. FOCKE, *California Institute of Technology.*—Bismuth single-crystals were grown in strong magnetic fields (10,000 gauss and more) by means of a special method which avoids any stress or pressure occurring in the generally known methods. The orientation between the axis of the crystals and the axis of the rod being predetermined by a seed-crystal and the orientation of the gradient of temperature. Three main orientations were studied.

1) Trigonal axis normal to the axis of the rod, normal to the lines of magnetic force ($\{111\}$ parallel to the field lines).

2) Trigonal axis normal to the rod. Parallel to the lines of force ($\{111\}$ normal to the field lines).

3) Trigonal axis parallel to the rod. Normal to the lines of force. ($\{111\}$ parallel to the field lines).

To obtain reproducible results the first half of the crystal was grown in general without, the second, with field. The density of the two halves was measured and it was observed that it was different in all cases when the crystal had the orientation 1) or 3). i.e. when the trigonal axis was normal to the lines for force. *The density of the magnetic half is larger.* The maximum change observed on good crystals until now is 0.10 gr. cm.$^{-3}$ Bragg-diagrams were taken of the corresponding planes of the two halves of a crystal which show a distinct change of the intensity of the different orders from the $\{111\}$ plane. The decline of the intensity with the order is smaller for the magnetic crystal than for the normal, which is especially expressed in the 4th order (K_α of Mo) which disappears almost entirely for normal bismuth (Ogg, Phil.

Mag. **42,** 163 (1921); James, Phil. Mag. **42,** 193 (1921)) and exists distinctly for the magnetic crystal. If this change of the parameter is accompanied also by a change in the spacing, indicated by a shift of the lines in the spectrum could not yet be settled. For the {111} planes, the lattice constant remains unchanged (within 0.1 percent).

27. Differences in the directions of ejection of x-ray photoelectrons from various atomic levels. E. C. WATSON AND J. A. VAN DEN AKKER, *California Institute of Technology.*—Magnetic spectra of photoelectrons ejected by x-rays from a very thin film, when taken *at different angles* by the method previously described (Phys. Rev. **30,** 479 (1927)) show large variations in the relative intensities of the various lines as well as the variations in absolute intensity already reported. Thus spectra of electrons emerging at 80° with the forward direction of the x-ray beam from a thin film of evaporated tungsten traversed by primary x-rays from silver show lines due to electrons from all three L levels; forward of 80°, the line due to the L_I electrons becomes gradually weaker relative to the other two lines and disappears in the forward direction; backward of 80°, the L_I line increases in strength relative to the other two. Similarly in spectra of electrons emerging from a silver chloride film traversed by primary x-rays from molybdenum, the lines due to electrons from the L_I level of silver and the K level of chlorine become gradually weaker relative to the line due to the L_{II} L_{III} electrons (unresolved) of silver as the angle is diminished from 80° to 0° and disappear in the forward direction, while they become relatively stronger than the $L_{II}L_{III}$ line as the angle is increased. Similar results have been obtained in other cases and for the M electrons. These results can only mean that the *directions of maximum photoelectric ejection are different for electrons from different atomic levels.*

28. The temperature dependence of electrical resistance. WILLIAM V. HOUSTON, *California Institute of Technology.*—To explain the fact that the resistance of a pure metal approaches zero with the absolute temperature, even though there is zero point energy of the crystal lattice, it is necessary to take into account the fact that all impacts of electrons with the lattice are inelastic and accompanied by a transfer of energy. The transfer of energy is restricted by the fact that the electron gas is degenerate, and that at low temperatures, many of the elastic oscillators are in the lowest possible energy states. When these restrictions are expressed as a transition probability, it is possible to derive a very satisfactory law of the temperature variation of resistance. Different metals will show a different variation for very low temperatures, but they will all lie between a variation with the first power and with the fifth power of the temperature.

29. Spatial distribution of photoelectrons ejected from a gas by x-rays. CARL D. ANDERSON, *California Institute of Technology.*—Photoelectrons ejected from the K level of the Br atom by x-rays of $\lambda = 0.586$A are studied by means of the Wilson expansion chamber to determine the effect of the binding energy of the scattering atom on the longitudinal space-distribution of the photo-electrons. In agreement with Auger (Comptes Rendus, **188,** 447, (1928)), the forward momentum of the photoelectrons is found to be proportional to $\nu - \nu_0$ to a first approximation. The average forward momentum, μ, of the photoelectrons can be expressed in the form $\mu = \sigma h(\nu - \nu_0)/C$ where the "asymmetry factor," σ, is equal to 1.5. Williams (Proc. Roy. Soc. **121,** 611, (1928)) and Auger (Comptes Rendus **187,** 1141, (1928)), working with light scattering atoms where ν_0 is negligibly small, have previously found values for σ of 1.3 to 1.4.

30. Ionization of nitrogen and air by positive ion bombardment. RICHARD M. SUTTON AND J. C. MOUZON, *California Institute of Technology.*—Previous work by one of us (Phys. Rev. **33,** 364, (1929)) showing positive ion ionization in argon and neon by potassium ions has been extended to the study of nitrogen and air. Both gases show the presence of ionization for accelerating potentials above 100 volts, at pressures between 0.1 and 0.7 mm. The abnormally high pressures indicate further evidence for the presence of long mean free paths for the positive ions. Secondary effects were investigated and duly accounted for. The calculated ionization at 750 volts in the gases studied to date, expressed as the number of ions formed per

initial positive ion per centimeter path reduced to one millimeter pressure, are: argon, 0.288; neon, 0.112; nitrogen, 0.124; air, 0.098; hydrogen, none detectable. These efficiencies are less than 4 percent of the electron ionization at the maxima for these gases (K. T. Compton and Van Voorhis, Phys. Rev. **26**, 436, (1925)).

31. Incoherent scattering and structure of diatomic molecules. F. RASETTI, *California Institute of Technology.*—Ultra-violet light from a mercury arc scattered by gases has been examined with a large quartz spectrograph. The fine structure of Raman spectra given by H_2, N_2, O_2, CO and NO has been analyzed. The result, in agreement with the theory outlined by the author in a recent paper, is that, when the molecule is in a S state (N_2, H_2, O_2, CO) only transitions with $\Delta j_k = 0, \pm 2$ can take place in the scattering process. In symmetrical molecules, if the nuclei have no spin (O_2) alternate rotational levels are missing, and this gives a pattern of equally spaced lines, the spacing being $8 \cdot h/8\pi^2 I_0$. If there is a nuclear spin (H_2, N_2) alternate weak lines are present; in H_2 the strong lines correspond to transitions between odd rotational levels, in N_2 between even levels. If the molecule is in a P state and has an electronic fine structure (^2P in the case of NO, $\Delta\nu = 124$ cm^{-1}) the transition between the two components of the doublet is observed in the Raman effect. This also is to be expected from the theory.

32. The magnetic properties of isolated ferromagnetic atoms. F. W. CONSTANT, *National Research Fellow, California Institute of Technology.*—In order to obtain a better knowledge of the elementary atomic magnet, its behavior when surrounded by non-magnetic atoms rather than by other magnetic ones has been studied. For this purpose, alloys of 90 and 95 percent platinum with the remainder cobalt and nickel, respectively, have been investigated and the cobalt ones found ferromagnetic. The magnetic moment per cobalt atom is greater than for pure cobalt. Var ous hysteresis loops, showing the relation between the magnetization and applied magnetic force have been obtained; heat treatment was found important, the wires in the hard drawn state showing considerably more hysteresis for the 95 percent Pt alloy, but after sufficient annealing, these more isolated magnetic atoms gave, conversely, less hysteresis. This last result is in agreement with Heisenberg's theory of ferromagnetism, based on resonance between the electrons of neighboring ferromagnetic atoms, this resonance decreasing as the ferromagnetic atoms are more isolated. Variation of magnetization with temperature and Curie points were also found, the latter falling rapidly as the cobalt content decreased, so that most of the measurements on hysteresis were made at liquid air temperatures.

33. The valence of sulfur in dithionates. RALPH WINGER, *California Institute of Technology.*—Lindh has shown that sulfur compounds show large shifts in wave-length of x-ray absorption edge, the main effect being due to chemical valence. It has been a question whether the two sulfurs in the dithionates (XS_2O_2) are in the valence states S_{II} and S_{VI}, as is generally assumed for the thiosulfates (XS_2O_3), or whether they are in the same state. If valence is calculated in the usual way, a value of V is obtained for the dithionate on the assumption that the sulfurs are equivalent. X-ray absorption data have been secured, showing the edge lying about halfway between the mean values for the 4- and 6-valent compounds. This indicates a valence of V for sulfur in the dithionates.

34. The electric moments of CH_3 and Br radicals in certain organic molecules. C. R. DAILY, *California Institute of Technology.*—As a further test of the Debye theory of binary liquid mixtures, the electric moments of various molecular combinations of CH_3 and Br radicals were determined from observations in binary mixtures with benzene of the dielectric constant, index of refraction, and density at various concentrations. The values obtained were: toluene 0.50×10^{-18} esu; brombenzene 1.70×10^{-18} esu; p-bromtoluene 2.15×10^{-18}; esu n-propyl bromide 2.00×10^{-18} esu; iso-propyl bromide 2.20×10^{-18} esu; ethyl bromide 2.12×10^{-18} esu.

Since the moment of Br is negative with respect to CH_3, p-bromtoluene should have a moment equal to the vector sum of the moments for toluene and brombenzene and close agreement is obtained. n-propyl bromide, iso-propyl bromide, and ethyl bromide have approximately the same moment which agrees with structural considerations of these molecules.

35. The electric volume-effects in bismuth single-crystals grown in strong magnetic fields. A. GOETZ AND M. HASSLER, *California Institute of Technology.*—The effect of strong magnetic fields on the electric volume effects (conductivity and thermo-electric effects) was studied on crystals which were grown one-half with the magnetic field and one-half without. There exists a thermo-electric force between both halves although there is no visible change in orientation. Besides, of this e.m.f. there is an e.m.f. which depends on the gradient of temperature, i.e. it depends on the heat-flow through the intersection between the magnetic and unmagnetic half. The conductivity of the two halves is also different. The changes of the volume effects depend on the orientation in which the crystal enters the field, which adds so much to the complexity of the matter that it cannot be described briefly.

36. A relation between lattice energy and shift in x-ray absorption edges. RALPH WINGER, *California Institute of Technology.*—Aoyama, Kimura, and Nishina have given a theory for the displacements of the x-ray absorption edges in certain chlorides having similar crystal structure and chemical binding. A consequence of their theory is that the shifts in frequency of the edges should be a linear function of the lattice energy. They have drawn a straight line through the few experimental points they were able to determine, but the points were too close together to furnish a convincing check. New points have been determined by using tetramethyl and tetraethyl ammonium chloride. The range of values is more than doubled, and the results show in general a progressive shift in frequency with increasing lattice energy. The new points lie roughly on a straight line which has a somewhat less steep slope. A straight line can be drawn through all the points within experimental error, but a curving line fits better. The theory seems too simple and there are probably other factors entering in.

37. Preliminary note on coefficients of relativity. S. R. COOK, *College of the Pacific.*—Coefficients in Lorentz's and Einstein's first paper are compared. The coefficients are then deduced from the difference between the paths of light in the Michelson-Morley interferometer experiment. It is shown that the coefficients deduced from the Michelson-Morley interferometer experiment correspond with those first deduced by Einstein, but differ from the Lorentz coefficients and from the coefficients finally deduced by Einstein and generally accepted by writers on relativity. It is further shown that wherever there is a transverse space coefficient there is a corresponding transverse time coefficient. The question is raised as to adequacy of the space and time coefficients most generally used by writers, and it is suggested that the more general coefficients first derived by Einstein and derived by the writer from the Michelson-Morley experiment would be more in accord with the facts of the Michelson-Morley experiment and with the genius of Einstein's theory of relativity.

38. Speech-power of speakers in auditoriums. V. O. KNUDSEN, *University of California at Los Angeles.*—Measurements of the speech-power of speakers indicate that the loudness of speech in auditoriums is considerably below the loudness level required for optimal hearing conditions. The average speech-power of six male speakers in a small auditorium (770 cu m) was 27.4 microwatts, and the average for eight speakers (six males and two females) in a large auditorium (6790 cu m) was 48.9 microwatts. From these data and the total absorption in the rooms, the probable loudness of the average speaker in the smaller auditorium is 50.7 db and in the larger auditorium 45.7 db. The optimal loudness for the hearing of speech is 70 db. The advantage of suitable speech amplifiers in large auditoriums is thus apparent. These data, together with known data on the interfering effect of noise and reverberation, make it possible to assign a quantitative rating to the hearing conditions in any auditorium. A series of curves gives the probable percentage of speech articulation in auditoriums of different sizes and times of reverberation. These curves also give the optimal time of reverberation for the hearing of speech in auditoriums, which varies from 0.80 seconds in small rooms to 1.50 seconds in very large auditoriums.

39. Classical scattering in x-ray reflection. PAUL KIRKPATRICK AND MARGARET DEWAR, *University of Hawaii.*—The classical treatment of the scattering of short wave-length radiation by electrons shows that the scattered intensity from an unpolarized primary beam should vary

as $(1+\cos^2 2\theta)$, where 2θ is the angle of deviation. We have investigated the validity of the expression in parentheses in its application to crystal reflection. Effectively unpolarized x-rays were reflected by a rock-salt crystal and the reflected beam allowed to strike an aluminum scatterer. The intensity distribution of the scattered radiation revealed the polarization imposed upon the reflected beam by the process of reflection, and this polarization was compared with that predicted by the classical scattering function. For deviations of 15°08′ and and 20°10′ the observed scattering is, within the limits of experimental error, classical. Reflection-scattering at deviations of zero and ninety degrees may also be shown to harmonize with these results, in the former case by symmetry and in the latter by reference to the observations of Mark and Szilard, (Zeits. f. Physik **35,** 743 (1926)).

40. The temperature coefficient of radioactive disintegration. OSCAR KNEFLER RICE, *National Research Fellow, California Institute of Technology.*—It is shown that the negligible temperature coefficient of radioactive disintegrations is what is to be expected from the known sizes of atomic nuclei, on the basis of the new quantum mechanical explanation of radioactivity. According to this explanation the alpha-particle in the nucleus which is to decompose is in some "discrete" state in the nucleus, but can leak out over a potential energy hump and appear in a continuous state outside the nucleus. If there is to be no temperature coefficient to such a process the alpha-particle must always be in its lowest state when in the nucleus. The energy to the next state can be calculated roughly from the size of the nucleus, and is shown to be so great that the probability that the alpha-particle will be in an excited state may be neglected, whence our proposition follows.

41. The mechanism of the spark discharge. L. J. NEUMAN, *University of California.*—It is well known that in a self-sustained electrical discharge it is necessary that electrons be liberated from the neighborhood of the cathode by some mechanism in addition to the cumulative ionization of the gas by electrons. Let us classify the possible mechanisms as follows: Those dependent on (a) the gas and velocity of the positive ions; (b) the gas, cathode material and the velocity of the positive ions; (c) the gas and cathode but *independent* of the velocity of the positive ions. A special discharge tube (Proc. Nat. Acad. Sci. **15,** 259 (1929)) was used to distinguish between these mechanisms experimentally. Assuming that most of the positive ions pass through the grid it has been shown that: (a) In A at low pressures the cathode material plays an important part in the mechanism of the spark discharge, as was previously observed by Holst and Oosterhuis, and J. Taylor; (b) under these conditions the principal mechanism producing electrons depends upon the *energy of impact of the positive ions with the cathode*; (c) as the pressure increases the predominating electron-producing mechanism changes from type *B* to *A* and the sparking potential becomes practically independent of the cathode material.

42. An electro-mechanical frequency analyzer. L. P. DELSASSO, *University of California at Los Angeles.*—For certain purposes in the study of complex sounds, analyzers which determine the amplitude and frequency of the components but not their phase relations are found useful. In this instrument the complex sound to be analyzed is converted, by a condenser microphone and a high quality amplifier, into potential fluctuations which are impressed on the quadrants of a modified quadrant electrometer. The needle of the electrometer is suspended by three fine tungsten wires forming a sharply resonant mechanical circuit. The period of this circuit is made continuously variable by changing the angular separation and tension of the suspensions. Vibrations of the mechanical circuit occur whenever its natural period agrees with the period of a component of the complex sound to be analyzed. The amplitude of the component is found from the amplitude of vibration of the needle and the frequency of the component from the tension on and angular separation of the suspensions. Frequency ranges of from 10 to 200 d.v./sec. and from 100 to 1700 d.v./sec. have been obtained. The work has been done with the help of a grant from the Guggenheim Fund for the Promotion of Aeronautics and is a part of an investigation to determine the practicability of using acoustic methods to measure the altitude of aircraft.

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